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ALUMINUM AS A FACTOR IN SOIL ACIDITY

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BY

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ALUMINUM AS A FACTOR IN SOIL ACIDITY

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I. INTRODUCTION

In 1902, the late Dr. Cyril G. Hopkins (33) and his associates of the Illinois Experiment Station presented at the nineteenth annual meeting of the Association of Official Agricultural Chemists the first practical method for ascertaining quantitatively the acidity or lime requirements of a soil. The method is based on the theory that the acids, organic and mineral, in the soil are insoluble in water and cannot be extracted with water, but when a mineral salt solution is added to the acid soil, a double decomposition takes place, the acids (humic acids) react with the salt solution, uniting with the mineral base, forming neutral humates and liberating the mineral acid or an acid salt. The titration of the mineral acid serves as a basis for determining the total acidity of the soil. Eichhorn (16) found that soil rich in humus and containing free humic acids, liberates the acid from neutral salt solutions when brought in contact with such a soil. Solenow (64) also observed that the difficultly soluble organic acids of the humus liberate mineral acids which may affect the plants growing on the soil affected. These observations are at variance with that made by Knop and Detmer (69) who claim that generally "humates" and "humic acids" are much less soluble in salt solutions than in pure water. But Heiden and Schumacker (37) demonstrated that portions of salts in solution are removed by peat, prepared humic acids, and artificial humus when these come in contact with the salt solution. Veitch (80) is also of the opinion "that organic matter is able to remove from solution a portion of the mineral salt with which it is brought in contact," but further asserts that "none of the standard works on absorption of soils makes mention of the production of free mineral acids; neither theoretical considerations nor a cursory examination of the literature lead one to believe that mineral acids in amounts equivalent to the total organic acids are set free by the action of mineral salt solutions on acid organic material."

Shortly after the publication of the Hopkins method of soil acidity-determinations, Veitch (80) subjected it to a critical study. Tests were made for free hydrochloric acid in the extract, and except in one or two cases where the presence of water-soluble sulfuric acid was proven, there were no tests which showed a considerable amount of free acid. Tests for phosphoric acid gave a negative result. In a previous work on the solubility of soil ingredient

in saline solutions, Veitch, however, noted the filtrates were frequently acid in reaction, and attributed it to the presence, in considerable quantities, of aluminum, iron and manganese in the solution. He further found that when the apparent acidity of the extract was equivalent to more than 1 or 2 cc. 0.05 *N* alkali a precipitate was formed on titration which he identified as the hydroxides of aluminum, iron and manganese. Ames and Schollenberger (3) by experiment undertook to demonstrate that free acid is formed by interchange, between acid soils and potassium nitrate solution. The procedure is described in Bulletin 306 of the Ohio Agricultural Experiment Station. The results obtained from 200 cc. of the potassium nitrate extracts are the following:

Acidity due to free acid, by titration with methyl orange.....	9.1 cc. 0.1 <i>N</i> NaOH
Total acidity to phenolphthalein.....	39.9 cc. 0.1 <i>N</i> NaOH
Acidity due to salts of Fe and Al (by difference).....	24.8 cc. 0.1 <i>N</i> NaOH
Chlorine equivalent to 0.3 cc. 0.1 <i>N</i> AgNO ₃	0.0476 gm.
Silica, by loss after HF treatment.....	0.0005 gm.
Ferric and aluminum oxides.....	0.0471 gm.
Iron by reduction and titration as Fe ₂ O ₃	0.0136 gm.
Al ₂ O ₃ by difference.....	0.0335 gm.
The iron was found equivalent to 5.0 cc. of 0.1 <i>N</i> NaOH; and the alumina to 19.7 cc.	

It is thus seen that although free acid has developed the acidity due to the presence of aluminum is more than twice the acidity due to free acid. The following opinion by Veitch (80) fits well with this result as well as with his own: "It seems that there is no setting free of appreciable quantities of hydrochloric acid, and that there is practically no reaction between the organic matter and the salt solution, whereby difficultly soluble organic acids are dissolved, but that the acidity of the filtrate (or the acidity which is greater than would be given by water under the same condition) is due to the solution of alumina or some other acid-salt yielding base."

The author has also made some studies on the composition of potassium nitrate extracts of three acid soils. A more detailed account of the results of this study will be given in the latter part of this paper, but the conclusion he reached is that potassium nitrate solution brings into solution the aluminum in the acid soil when the latter is brought in contact with the salt solution; that the strong acidity exhibited by the potassium nitrate extract is due largely to the presence of a considerable amount of aluminum in solution; and that the precipitate formed at the point when the extract passed from an acid into an alkaline solution is largely aluminum hydroxide.

Hitherto, the significance of Veitch's discovery has never been appreciated, and the nature of soil acidity has generally been ascribed to the presence of free organic and mineral acids in the soil. The recent work, however, of such men as Abbott, Conner and Smalley (1) of Indiana, Ruprecht and Morse of Massachusetts (59) and Hartwell and Pember (27) of Rhode Island, in which they have shown the rôle aluminum plays in some acid soils, has given a new phase to the problem of soil acidity. The last two men, especially, are so

convinced of the presence of aluminum in acid soils as the cause of the different behavior of barley and rye grown in an acid soil that they think "the elimination of the effect of aluminum in acid soils seems likely to prove more important than the neutralization of the acidity" and that "attention should be given to methods of determining active aluminum while we are also developing those for soil acidity" (28). If aluminum should prove to be the most important factor in acid soils, and a search is made for a method for determining active aluminum and for eliminating its effect in acid soils, such a method already exists. Veitch had demonstrated that the Hopkins method does not bring considerable free acids in an acid soil into solution but instead brings the aluminum in the soil into solution; the application of the method to field conditions has brought excellent results. In other words, the method determines aluminum. The application of limestone to acid soils, according to the method, eliminates the effect of aluminum, and so far as aluminum is concerned in acid soils the Hopkins method is the best method for determining and correcting soil acidity.

II. OPINIONS CONCERNING THE CAUSE AND NATURE OF SOIL ACIDITY

Frear (19) and Ames and Schollenberger (3) have already reviewed quite comprehensively the literature and theories covering the subject of soil acidity and in this paper the author only attempts to summarize briefly the opinions expressed by the different investigators. These opinions or theories may be divided into three groups.

1. The presence of true acids.
2. Adsorption by soils.
3. The presence of considerable quantities of soluble aluminum salts.

1. The presence of true acids

In this group there are two important theories, the organic acid theory and the mineral acid concept. Let us take up first the organic acid theory.

In the decomposition of plant and animal residues organic acids are produced. Under proper aeration these decomposition products are used up by soil organisms as fast as they are formed. But in poorly aerated and drained soils, these products may accumulate giving rise to acid condition. The acidity of some peat and muck soils has long been known, and this acidity has been assigned to complex insoluble organic acids. This theory was proposed by Sprengel (65) after having discovered what he called humic acid. Berzelius (6) further advanced the theory when, by treating a soil with an acid he obtained two substances, one insoluble and the other soluble, the latter being identical to the humic acid of Sprengel. Tacke and Süchting (71) held the view that the acidity of humic acids can only be accounted for on the basis of true acids. That organic acids exist in normal soils is a known fact. Blair and Macy (8) in Florida found muck soils which gave an acid aqueous extract

after boiling the extract for a long time. They ascribed the acidity to soluble organic acids in the soil. The so-called humus has been subjected to a critical examination by Shorey (63) who found thus far at least thirteen organic acids, among which are oxalic acid, succinic acid, saccharic acid, acrylic acid, picoline carboxylic acid, paraffinic acid and lagnoceric acid. But it is believed that under ordinary conditions the organic substances present in the soil cannot bring a condition unfavorable to plant growth.

Some soils while deficient in organic matter are decidedly acid, hence it follows that the acidity in this case must be attributed to other causes. Truog (75) thought that the acidity in this case is caused by true acids. It is claimed that plants and certain hydrated compounds in the soil removed the bases from the salts leaving free acids. Stoddart (67) for example, is of the opinion that the sulfates and chlorides in the soil are split up, the base elements being absorbed by the plants, leaving the acid radicals as acids thus giving rise to an acid condition. It is further believed that the silicates which are important constituents of soils of non-limestone rock origin are decomposed by carbonated water in the soil resulting in the removal of bases which are either taken up by plants or leached out. The oxides of silicon and aluminum left over combine to form aluminum-silicic acids which may cause soil acidity. Truog (77) says: "It is possible that mere removal of bases from the original silicates may give rise to acid silicates which cause soil acidity." On this point Hopkins (32, p. 176) says, "Acid silicate is formed from polysilicates from which some basic elements may have been removed and replaced with acid hydrogen, by reaction with soluble organic acids, or possibly by the long-continued weak action of drainage waters charged with carbonic acid, do exist in the soil, and the evidence thus far secured indicates that they account for most of the acidity of soils which are at the same time strongly acid and very deficient in humus." In the study of acid red clay soils of Porto Rico, Loew (41) ascribes the acidity to the presence in the soils of an acid clay or aluminum silicates having the formula $H_4Al_2Si_2O_9$, which he called argillic acid.

Lastly by the use of electrometric and colorimetric methods of determining hydrogen-ion concentration, Gillespie (22) demonstrated the presence of acid in the soil. His findings were in accordance with the results of Sharp and Hoagland (62), who concluded that soil acidity is due to the presence of an excess of hydrogen ions in the soil solution.

It is believed that certain treatments of the soil may also give rise to acidity in the soil. Continued application, for example, of artificial fertilizers like sulfate of ammonia and acid phosphate causes acidity of the soil. When sulfate of ammonia is applied to soils, ammonia is nitrified leaving the sulfate radical to form sulfuric acid. Muriate of potash, according to Stoddart (67) tends to leave an acid residue due to the absorption of potassium by plants or soil colloids, leaving free sulfuric and hydrochloric acids. There are instances in which continued application of ammonium sulfate to the soil resulted in an acid soil. Wheeler (82) reported acid the soil in the plots of the Rhode

Island Experiment Station which received ammonium sulfate continuously. Hall and Gimingham (24) in England, Hunt (35) in Pennsylvania and Ruprecht and Morse (60) in Massachusetts encountered similar results with experimental plots receiving ammonium sulfate continuously but not limed.

It has also been thought that acid phosphate may produce acidity in the soil. The fact that acid phosphate is an acid salt is responsible for this belief. In discussing the advantages of raw phosphate over acidulated phosphate Hopkins (32, p. 242) says: "A third point in favor of raw phosphate in common with bonemeal and slag, is that it is free from acidity and has no tendency to injure the soil. This is a minor advantage, because if acidity develops from the use of acid phosphate (and it does) it can be corrected at a small expense by the addition of any form of lime." Thorne (72) of the Ohio Experiment Station also is of the opinion that acid phosphate may develop acidity in the soil. He says: "There is reason to believe that acid phosphate increases the tendency to soil acidity, but it is not the sole cause of such acidity for there are very acid soils which have never received any phosphate." These opinions, however, do not agree with the experimental evidence. In a study of the acidity of experimental plots in Indiana in which acid phosphate has been applied for twenty years, Conner (13) found that these plots show less acidity than soils which have never had acid phosphate. By computing the amount of free phosphoric acid added to the soil when the rate of application is 200 pounds of acid phosphate containing 14 per cent available phosphoric acid, Frear (19) concluded that it would take a long time and a large amount of phosphate to make a soil acid by such direct action. The results of the author's tests which will be presented in this paper also indicate that acid phosphate tends to reduce rather than increase the acidity of the soil.

2. The adsorption theory of soil acidity

The phenomenon of soil acidity has also been explained as a case of adsorption. Cameron (11) was the first to apply the theory of adsorption in explaining the acid reaction of certain soils. He attacked the blue litmus paper test for soil acidity on the ground that wet cotton also turns blue litmus paper red. He is of the opinion that the reddening of blue litmus paper by certain soils is a case of selective adsorption.

After investigating some acid soils of Michigan, Harris (25, 26) arrived at the conclusion that the acid reaction of the soil is due to selective adsorption and not to the presence of acids.

Parker (49) asserts that because of the nature of the surface of its constituents soils adsorb the cation at a greater rate than the anion, and that the acid reaction of certain soils is due to this fact.

In a comprehensive study of acid soils of Japan, Daikuhara (14) concludes that their acid reaction is not due to organic acids (humus) alone but also to adsorption of colloidal compounds of aluminum and iron.

Gully (23) also ascribes the acid reaction of peat moss and peat soils to adsorption of the colloidal matter of the covering of the sphagnum cells.

3. The presence of soluble salts of aluminum in the soil

The idea had its inception in the work of Abbott, Conner, and Smaller (1) who investigated a few years ago, the causes of the unproductivity of some soils in Indiana. They obtained water extract of the acids soils, and determined its composition. They have found that the extract reacts acid to phenolphthalein and that the nitrate was present partly as aluminum nitrate. Corn seedlings were grown in the extract along side of solutions of nitric acid and aluminum nitrate of known normality, and it was found that the extract was extremely toxic up to 0.0005 *N*. It was found that the toxicity of the extract was equal to the toxicity of nitric acid and aluminum nitrate of the same normality; and the conclusion arrived at was that soluble salts of aluminum are largely responsible for the unproductiveness of the soils in question.

Ruprecht and Morse (60), investigating the effect of continued application of ammonium sulfate to soils, found that aluminum sulfate is formed which causes the acid reaction and the unproductivity of the soil.

Hartwell and Pember (27) carried on a comprehensive search for the cause of the different behaviour of rye and barley grown on soils from plots continuously receiving ammonium sulfate. Different inorganic substances have been subjected to experiment to discover the most active factor and the conclusion reached was that aluminum is the element responsible for the depression of the growth of barley.

After reviewing the different theories concerning the nature and cause of soil acidity Ames and Schollenberger (3) expressed the following opinion: "The theory of the existence of silicic or alumina-silicic acids in the soil would serve as a complete explanation for all the observed phenomena; the conception is simple and is supported by analogy with better known reactions which is as much as can be said for any of the theories which have been offered."

The work of Abbott, Conner and Smalley, Ruprecht and Morse, and of Hartwell and Pember, however, has opened up new possibilities by which the nature and causes of soil acidity could be studied further. With the hope that more light might be thrown upon aluminum as a factor in soil acidity the present work has been undertaken, bearing in mind three facts. First, aluminum salts are highly toxic at a certain concentration; second, aluminum is abundant in the soil, being next to oxygen and silicon; and third, plants absorb bases and calcium carbonate is leached out of the soil resulting in the depletion of the soil of this compound and enabling the aluminum in the soil to act as a base.

III. ALUMINUM IN AGRICULTURE

Aluminum is universally known as a non-essential element to plants. Hydrated silicates and oxides of aluminum, however, are believed to exercise great influence in holding some of the plant-food elements in the soil, preventing their loss in drainage water. Aside from this, aluminum has no economic

value in agriculture. As stimulants or as fertilizers very little is known of aluminum compounds and the few scattered experiments on this subject are incomplete and inconclusive. On the other hand, aluminum has been found extremely toxic to plants. Since aluminum is abundant in the soil and under certain conditions becomes harmful to plants, as in the case of some acid soils, it is in this fact that aluminum will prove of great importance to the agriculturist.

Aluminum in plants

Although aluminum is not an essential element, analyses of ashes show that it is taken up by plants. It is, however, present in small amounts in most plants. Pfeffer (50) speaks of the abundance of aluminum in *Lycopodium chamaecyparissus* and *L. alpinum*, where it constitutes from 22 to 27 per cent of the ash, while in certain species of *Lycopodium* only traces are found. Johnson (37) states that aluminum is found in small amounts in the ashes of agricultural plants, but added that it is not clear whether it is an ingredient of the plants or due to particles of clay adhering to plants. Robinson, Steinkoenig and Miller (57) report analyses of legumes, vegetables, grasses, trees, shrubs, and show that aluminum is found in all the plants analyzed. The form in which aluminum is present in the plant is not known. According to Berzelius, aluminum as alumina is united with tartaric acid, and according to the Ritthausen with malic acid [quoted by Johnson (37)]. Pfeffer (50), however, is not certain whether aluminum in *Lycopodium* is present in the form of tartrate. In a study of the aluminum contents of certain vegetables including corn and corn products, hominy, oatmeal, carrots and white and sweet potatoes, Meyers (44) found that aluminum in these vegetables is found in a soluble form, and averred that a relatively large consumption of aluminum may result from a diet consisting chiefly of vegetables.

Physiological action of aluminum on plants. According to Jost (38) Jamano found aluminum to be of service in the development of barley. This is in conflict with the results of Hartwell and Pember (27), in which they show that the depression of the growth of barley in an acid soil is due to the presence of aluminum. Maze (43) also asserts that aluminum is necessary for the best growth of maize. Experimental evidences, however, point to the fact that aluminum is not only a non-essential element but it is also very harmful to plants under certain conditions.

Fluri (18) describes certain experiments carried out on *Spirogyra*, *Elodea*, and *Lemna* with sulfate, nitrate, chlorate and bichromate of aluminum. He found that in light, production of starch is reduced, but also found that while assimilation was checked it was not inhibited. The aluminum found in the cell was small and the action could not then be attributed to a chemical reaction. But as starch production was affected it was thought that the action of aluminum was on the diastase.

Hebert (29) made some germination tests of peas, wheat and rape with sulfates of aluminum and other metals and found that the salts were strongly

poisonous. Varvaro (79) also reports that aluminum oxide, like the oxides of manganese, iron, uranium, cerium, copper, zinc, cadmium, mercury and lead has a retarding effect on the germination of kidney beans, but has an accelerating effect in the case of corn. Experimenting on the effect of different aluminum salts on the germination of wheat, Micheels and DeHeen (45) found that while kaloin and alumina were somewhat beneficial, the salts were very harmful.

In investigating the effect of different salts of aluminum on the growth of *Zea mays*, *Vicia faba*, *Leus esculenta* and *Helianthus annuus* Kratzmann (39) found that the growth was hindered by the salts when the concentration was 0.005 per cent, but stimulated when the concentration was only 0.0001 per cent. Aluminum nitrate showed a toxic effect. In this connection, significant is the statement of House and Gies (35) that the toxicity of aluminum salts depends upon the concentration of the solution. Yamano (84) found that moderate amounts of aluminum salts have a stimulating effect upon the development of barley and flax. He further found that in water culture 0.2 per cent of alum proved injurious after three weeks while 0.8 per cent killed the plant in a few days. Miyake (46) also found that the aluminum chloride is toxic even in dilute solution. The toxicity appeared when the concentration was greater than 0.000133. It was further found that the toxicity of aluminum chloride was approximately equal to that of hydrochloric acid of the same normality. Under the supervision of Professor C. F. Hottes of the Department of Plant Physiology, the author carried on some experiments on the toxicity of aluminum sulfate to barley. Solutions of 0.01 *N*, 0.001 *N*, 0.0001 *N*, and 0.00005 *N* were prepared, and barley seedlings were grown in them. The author found that the average growth of 10 plants for 7 days was 70.5 mm. in the control; 45.5 mm. in 0.01 *N*; 65 mm. in 0.001 *N*; 71.5 mm. in 0.0001 *N* and 78.9 mm. in 0.00005 *N*. It is thus seen that 0.01 *N* is highly toxic; 0.001 *N* depresses growth; and 0.0001 *N* has no effect at all. In 0.00005 *N* stimulating effect was noted. It was further observed that the seedlings growing the first two dilutions had root systems more than three times as greatly depressed as those growing in the control or in any of the two weaker solutions. The limit of toxicity lies probably between 0.0001 *N* and 0.001 *N*.

Other investigators who have proved the toxicity of aluminum salts are Abbott, Conner and Smalley; Ruprecht and Morse; and Hartwell and Pember, whose works have been already mentioned in the preceding discussion. It may be said, however, that it was not until the work of these men appeared that the toxicity of aluminum salts has been linked with the soil as a contributing factor in soil acidity.

Aluminum salts as stimulants and fertilizers

Experiments have been made to ascertain the value of aluminum salts as catalyzers or stimulants. Pfeiffer and Blanck (51) found that small amounts of aluminum sulfate combined with a small portion of manganese sulfate

caused an increase in the yield of dry substance in the grain, but an increase of the salt reduced the yield. Stoklasa (68) reports results from experiments on catalytic fertilizers for sugar beets. He showed that a combined application of 9 kgm. (19.8 lbs.) of manganese and 4.48 kgm. (9.8 lbs.) of aluminum sulfate per hectare has increased the yield of sugar beets from 30 to 50 per cent. He is of the opinion that aluminum, like manganese, zinc, and copper, is a catalytic agent, performing a function in the assimilation of carbon by promoting rapid photosynthesis. Boullanger (9) made a comparative study of the catalytic value of the sulfates of aluminum, manganese, ferrous iron and uranium, and found that while the results obtained were not uniform, in the majority of cases they increased the yield. In the case of aluminum nitrate, however, the experience of Munerate, Mezzadrolì and Zapparole (47) was different. They carried on a comparative test of the stimulating value of aluminum nitrate and sulfate together with the sulfate, chloride, dioxide and carbonate of manganese, boric acid, borate of soda and sulfate of uranium. The results showed that the lowest yield of sugar beets was obtained in the plot which received 100 kgm. (220 lbs.) per hectare of aluminum nitrate.

An attempt has been made also to find the effect on the productivity of the soil by the application of aluminum silicates. Voelcker (81) reports pot culture experiments in which green manures were associated with aluminum silicates, sodium silicates, kaolin, lime and magnesia. The results obtained showed that kaolin did not increase the yield of crops, but aluminum silicates with mustard as a green manure caused a large increase in the crop.

Finally, experiments have been carried out to determine the value of insoluble aluminum phosphate as a source of phosphorus to the plants. Pri-anishnikov (52) describes sand culture experiments in which wheat, oats, barley, peas and buckwheat were fertilized with aluminum phosphate alone and with calcium carbonate. The conclusion reached was that aluminum phosphate is assimilated, and that calcium carbonate had no appreciable depressing effect on the assimilability of aluminum phosphate. Baguley (4) reports a comparative test of orthophosphates of iron, calcium and aluminum on oats, peas and Swedish turnips grown on sand and chalk. The results obtained were better with iron and aluminum phosphates than with calcium phosphate. Truog (74) also presents results of experiments carried out in the greenhouse with ten different kinds of plants manured with rock phosphate, precipitated calcium phosphate, and phosphate of aluminum, iron and manganese. The results obtained were summarized as follows: "Contrary to the general belief that aluminum and iron phosphates are relatively unavailable to plants, nine of the ten plants tested made better growth on aluminum phosphate than on calcium phosphate, and six better growth on iron (ferric) phosphate." In another publication (76) in which results from a more comprehensive series of experiments on phosphate involving a large number of plants, were presented, he draws this conclusion: "Precipitated ferric and aluminum phosphates produced with a few exceptions good growth and in a few cases even better growth than the acid phosphate."

Aluminum in the soil

Aluminum is the most widely scattered metal (53) and next to oxygen and silicon is the most abundant element. It constitutes 7.85 per cent of the lithosphere and 7.30 per cent of the lithosphere and atmosphere combined (12). It does not occur in nature in the free state, but in combination with oxygen, the alkalis, flourine, silicon, the acids, etc., it forms minerals and rocks which on disintegration become the bases of soils and clays. Aluminum is present in the soil as the oxide, hydroxide, hydrated oxides, phosphate and silicates (64). In order to give some idea as to the amount of aluminum present in the soil, analyses of some soils in America are given in table 1.

TABLE 2
Chemical analyses of some American soils

CONSTITUENTS	ADOBE SOILS		COASTAL PLAINS PROVINCE	LIME- STONE VALLEY AND UPLAND PROVINCE	PIED- MONT PLATEAU PROVINCE	GREAT PLAINS PROVINCE	GLACIAL AND LOESSIAL PROVINCE	RIVER FLOOD PLAINS PROVINCE
	A	B	No. 1	No. 3	No. 15	(1)	(5)	(13)
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
SiO ₂	19.24	66.69	94.50	79.25	66.49	78.85	76.81	93.29
Al ₂ O ₃	3.26	14.16	2.07	8.89	17.11	9.68	9.73	2.45
F ₂ O ₃	1.09	4.38	0.83	4.44	7.43	2.72	3.26	0.78
MnO.....	Trace	0.09	0.007	0.07	0.51	0.036	0.068	0.066
MgO.....	2.75	1.28	0.09	0.33	0.31	0.72	0.60	0.01
CaO.....	38.94	2.49	0.39	0.63	0.36	0.94	0.92	0.15
Na ₂ O.....	Trace	0.67	0.11	0.24	0.16	2.02	1.74	0.03
K ₂ O.....	Trace	1.21	0.10	0.67	0.62	2.31	2.20	0.45
H ₂ O.....	1.67	4.94						
P ₂ O ₅	0.23	0.29	0.06	0.18	0.17	0.11	0.12	0.06
CO ₂	29.57	0.77						
Organic matter.....	2.96	2.00	1.13	1.96	1.26			
SO ₃	0.53	0.41	0.07	0.13	0.07	0.07	0.11	0.10
Cl.....	0.11	0.34						
Loss on ignition.....			1.74	4.80	8.06	2.28	4.09	2.12

The first two columns are adopted from Clarke (12), the next three from Robinson (55) and the last three from Robinson, Steinkoenig and Fry (56). The soil indicated A, is from Salt Lake City, Utah; B is from Santa Fe, New Mexico; No. 1 is Norfolk sandy loam, 3 miles southwest of Laurinburg, North Carolina, depth 0 to 14 inches; No. 2 is Decatur clay loam, 1 mile east of Holly-wood, Alabama, depth 0 to 4 inches; No. 15 is Cecil clay 2½ miles northwest of Charlotte, North Carolina, depth 0 to 6 inches; (1) is Colorado sand near Greeley, Colorado, depth 0 to 14 inches; (5) is Knox silt loam, 2 miles north of Farley, Missouri, depth 0 to 14 inches; and (13) is Cahaba very fine sandy loam, Minden, Louisiana, depth 0 to 12 inches. For further details about these soils the reader is referred to the publications of these men.

By recalculation the total aluminum in these soils per acre of 2,000,000 pounds of surface soil amounts to 34,576 pounds for Salt Lake City adobe; 151,181 pounds for Santa Fe adobe; 21,954 pounds for Norfolk sandy loam, North Carolina; 94,237 pounds for Decatur clay loam, Alabama; 181,469 pounds for Cecil clay, North Carolina; 102,666 pounds for Colorado sand; 103,196 pounds for Knox silt loam, Missouri; and 25,985 pounds for Cahaba very fine sandy loam, Louisiana.

Burd (10) also reports total analyses of certain silty clay loam and fine sandy loam soils in California in which, for example, one silty loam soil and one fine sandy loam soil contain 14.03 per cent and 16.73 per cent alumina, or 148,802 pounds and 177,438 pounds aluminum per acre, respectively.

Aluminum in the subsoil. Analyses of the subsoils of soils given in the preceding table show larger quantities of aluminum. For example, the subsoil of Decatur clay loam contains 3 per cent more alumina than the surface soil. In every one of the ten subsoils analyzed by Robinson (55) alumina is higher than in the surface.

TABLE 2
Alumina in soil separates

SEPARATES	HEAVY LOAM	LOAMY LOESS SOIL	COARSE SANDY GNEISS SOIL
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Coarse dust, 0.25 to 0.01 mm.....	1.63	7.28	18.71
Medium dust, 0.01 to 0.005 mm.....	15.20	14.20	24.20
Fine dust, 0.005 to 0.0015 mm.....	20.48	19.41	30.21
"Clay" (Schlamm), 0.0015 to 0 mm.....	27.76	29.97	32.42

Distribution of aluminum in the soil separates. There have been a few attempts to determine the distribution of the chemical constituents of the soil in the different soil separates. Puchner, quoted by Failyer, Smith and Wade (17), presents data of chemical analyses for separates of three types of soil. The percentage of alumina found is given in table 2.

Steinkoenig (66) also reports determination of certain constituents of separates of ten loam soils from New York, North Carolina, Pennsylvania, South Carolina, Virginia, New Hampshire and Wisconsin. The average alumina found in the separates of these soils, together with the maximum and minimum is given below:

	FINE SAND	COARSE SILT	FINE SILT AND FINE CLAY
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Average.....	5.48	8.44	22.57
Maximum.....	12.56	18.28	31.33
Minimum.....	0.40	1.48	16.76

From the data above it can be seen that the largest quantity of aluminum is found in the finest particles of the soil and that the quantity diminishes as the particles become coarser. It follows from this fact that the more clayey the soil is the higher is the aluminum content, and this seems to be the case if the Cecil clay is taken as proof.

The aluminum compound in the soil that gives rise to soluble aluminum salts. Mention has been made before that aluminum is present in the soil as oxide, hydrated oxides, hydroxides, phosphates and silicates. But which of these compounds breaks up so readily in the soil to form soluble salts that proved injurious to crops in some soils, as has been found by Abbott, Conner and Smalley, and Ruprecht and Morse? We naturally look upon hydroxides. There are three forms of aluminum hydroxides recognized: Diaspore— $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, bauxite— $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, and gibbsite, otherwise called hydrargillite or oxyhydrates, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (53). Do these three forms behave chemically the same with mineral acids? Diaspore and bauxite are insoluble in cold and hot water and in acids and alkalies, but gibbsite, while not soluble in cold and hot water, is soluble in acid and alkalies (48). Moreover, the so-called aluminum salts, aluminum nitrate, $\text{Al}_2\text{O}_3(\text{NO}_2)_6$, aluminum acetate, $\text{Al}_2\text{O}_3(\text{C}_2\text{H}_3\text{O})_6$, aluminum sulfates, $\text{Al}_2\text{O}_3(\text{SO}_2)_3$, and aluminum phosphate $\text{Al}_2\text{O}_3(\text{PO}_4)_2$ —are chemically considered as derivatives of the oxyhydrates (53). Gibbsite, therefore, answers the first question, and the next question that comes up is, whether gibbsite is present in the soils of America.

Lateritization in northern climates. In the decomposition of rocks an insoluble residue made up mainly of silica, alumina and ferric oxide, and combined with water, is left over. When kaolinite is the predominant constituent of the residue it is called clay, but when hydrates of alumina and iron predominate the residue is called laterite. Hence, the process of rock decomposition in which kaolinite is the end product is called kaolinization and that process in which hydrates of alumina and limonite are the ultimate products is called lateritization (15). In regard to the latter process Clarke (12) says, "In the tropical and subtropical regions the processes of rock decay are often carried further than is usually the case within the temperate zones. The leaching is more complete, the silicates are more thoroughly decomposed, and the residues are richer in hydroxides."

There is a general opinion among geologists that kaolinization is characteristic of rock decomposition in northern climates while lateritization is characteristic of that in tropical and subtropical regions. For this reason there is a diversity of opinion as to the occurrence of aluminum hydrates in the soils of America. Cameron and Bell (11) for example, state that "either gibbsite or bauxite is but seldom found in soil," and that in the examination of several thousand soils from all over the United States, in only one soil, that which comes from southern California, was aluminum hydroxide observed. Lindgren (40) is also of the opinion that little or no aluminum hydroxide is formed in ordinary rock weathering, and that the occurrence of bauxite is a rarity in

the temperate climate. On the other hand, Edwards (15) by recalculating analytical data for clays from different states, shows that bauxite exists in 21 states besides those in which the mineral exists in deposits of commercial value. In regard to the independence of bauxite as a mineral species Lindgren (40) says, "The independence of bauxite as a mineral species, is, however, questioned and it is believed rather to be a mixture of diasporite and gibbsite. The Georgia bauxite according to T. L. Watson corresponds well to gibbsite." Hilgard (30) found a high ratio of alumina to soluble silica in some of the soils he examined, and could not attribute it to other than the presence of hydrous alumina, possibly gibbsite. Beyer and Williams (7) reporting the analyses of flint fire clays from Missouri and New Jersey, also found a higher ratio of alumina to silica than that found in kaolinite but attributed it to the presence of a more highly aluminous silicate which he called pholerite. In the reported analyses of ball and flint clays from Missouri and of fire clays from Pennsylvania, Rolfe (58), again, found a high proportion of alumina to silica, and attributed this to the presence in the clays of gibbsite or other minerals high in alumina. Ries (54) believes that there is the possibility that in kaolins high in aluminum bauxite or gibbsite might be present. Finally, Galpin (21) in the study of flint clays and their associates encountered highly aluminous fire clays from near St. Louis, Missouri, and proves that the excess of alumina to silica is due to the presence of gibbsite.

The author does not pretend to show that aluminum hydrates are of common occurrence in the soils in America, but with the evidence gathered from the works of the men mentioned above he can not help reaching the conclusion that in some soils in the United States hydrates of alumina are present, and that in the case of soils where sufficient amounts of soluble salts of aluminum are found to be harmful to crops, the aluminum compound furnishing the aluminum is gibbsite, and until further investigations prove the contrary the author will hold to this view.

IV. EXPERIMENTAL

The problem

The work reported in this paper has been undertaken with the view of gaining some information on the following questions:

1. Aluminum is found in the soil in abundance and in conditions of varying stability. When an acid soil is extracted with potassium nitrate solution aluminum is brought into solution and is largely responsible for the acid reaction of the extract. Is not the acidity of the so-called acid soil due to the presence of active aluminum in the soil?

2. Sweet clover does not grow on a strongly acid soil while other plants have their growth depressed. Since aluminum salts have been found highly toxic even in dilute solutions, is not this behavior a reaction to the toxicity of soluble salts of aluminum in the soil?

3. When acid soils are treated with limestone according to the potassium nitrate method, sweet clover thrives well. Does not calcium carbonate eliminate the toxicity of aluminum? And if so, how does it act?

4. Does acid phosphate increase the acidity of an acid soil?

5. If the acidity of the soil is due to the presence of active aluminum, what effects have soluble salts of aluminum on sweet clover grown in sand? What effect has aluminum salts on sweet clover in the presence of calcium carbonate, or acid phosphate?

General plan of the work

Based on the foregoing propositions, plans have been carried out:

1. To study the potassium nitrate extract of an acid soil before and after the application of limestone.

2. (a) To leach out a considerable quantity of acid soils with potassium nitrate and with water until the last 125 cc. of leachings no longer indicate acidity, and to grow crops on it.

(b) To analyze the leached out soils for aluminum, iron and manganese.

3. (a) To grow crops on acid soils, treated with limestone and acid phosphate, alone and in combination with each other, and in different amounts.

(b) To set aside a similar series as above, giving the same treatment except the growing of crops, for acidity determinations in two different periods.

4. To grow crops on sand treated with aluminum sulfate, aluminum chloride and aluminum nitrate and aluminum hydroxide, alone and in combination with calcium carbonate or with acid phosphate.

Description of the material used

Three types of soil have been secured from southern Illinois for this work. They are—gray silt loam, on tight clay of the lower Illinoisan glaciation area; yellow gray silt loam, an upland timber soil; and yellow silt loam from the unglaciated areas. All the soils were acid to the blue litmus paper test. The physical composition of these soils is given in table 3. The Bureau of Soil's method and grades of mechanical separation have been adopted in this analysis (42). Some of the chemical constituents of the soils are given also in column 2, table 4. Except for aluminum, iron and manganese, the methods of chemical analysis used were those of the University of Illinois Agricultural Experiment Station. Aluminum, iron and manganese were determined by a combination of some of Hillebrand's procedures and of some in Treadwell's "Qualitative Analyses." The sample was fused with sodium bicarbonate, and the subsequent steps as directed in Hillebrand's methods, were followed up to the point of precipitating aluminum and iron. The ammonium persulfate method was adopted at this point to precipitate the manganese together with aluminum and iron (31). Manganese was then separated from aluminum and iron by the barium carbonate method and determined as manganese

pyrophosphate as directed in Treadwell's process (73). Aluminum was separated from iron by the potassium hydroxide procedure and both were weighed as oxides, also according to the direction of Treadwell.

Gray silt loam. This is a surface soil taken from the border of one of the control plots of the experimental fields at Newton, Jasper County. It contains 98.24 per cent dry matter. The reaction as tested in the laboratory is acid, and the acidity or lime requirements according to the Hopkins method is 2125 pounds of limestone of 93 per cent purity, per acre (2,000,000 pounds of soil $6\frac{3}{4}$ inches). The amounts of essential plant-food elements found are: nitrate-nitrogen 26 pounds per acre; total nitrogen 2900 pounds; phosphorus 1104 pounds; potassium 25,130 pounds; calcium 4510 pounds; magnesium 4520 pounds; and iron 47,800 pounds. Besides these the soil contains 840 pounds of manganese and 121,000 pounds of aluminum per acre.

TABLE 3
Physical analysis of the soil (grades of Bureau of Soils)

CONSTITUENTS	SIZE OF PARTICLES	GRAY SILT	YELLOW GRAY SILT	YELLOW SILT
	mm.	per cent	per cent	per cent
Moisture.....		1.76	1.36	1.61
Fine gravel.....	2-1*	0.93	1.37	0.00
Coarse sand.....	1.0 -0.5	2.15	1.79	0.21
Medium sand.....	0.5 -0.25	5.77	2.57	0.44
Fine sand.....	0.25-0.1	10.93	4.09	0.97
Very fine sand.....	0.1 -0.05	25.26	20.72	52.35
Silt.....	0.05-0.005	44.61	50.99	19.54
Clay (by difference).....	0.005	10.15	18.45	26.47
Total.....		99.80	99.99	99.98

* Calculated on water-free basis.

Yellow gray silt loam. This was taken from the farm of Joseph Quiztell at Carmi, White County, Illinois. It contains 98.64 per cent of dry matter. The reaction is acid and the lime requirements amount to 2814 pounds of limestone per acre. The essential plant-food elements found amount to 36 pounds of nitrate nitrogen per acre; 1370 pounds of total nitrogen; 693 pounds of phosphorus; 35,800 pounds of potassium; 3920 pounds of calcium; 4180 pounds of magnesium; and 74,200 pounds of iron. The manganese and aluminum found amount to 786 pounds and 151,000 pounds, respectively.

Yellow silt loam. This was taken near Vienna, Johnson County. It contains 98.39 per cent of dry matter. The reaction is acid and the lime requirement amounts to 2921 pounds per acre. The essential plant-food elements run up to 60 pounds of nitrate-nitrogen per acre; 1966 pounds of total nitrogen; 691 pounds of phosphorus; 29,000 pounds of potassium; 7850 pounds of calcium; 5330 pounds of magnesium and 74,200 pounds of iron. Manganese and aluminum reached 660 pounds and 14,900 pounds per acre, respectively.

TABLE 4
Gray silt loam

DETERMINED	ORIGINAL		EXTRACTED WITH KNO ₃		EXTRACTED WITH H ₂ O	
Dry matter.....	98.24 per cent		98.15 per cent		98.28 per cent	
	P.p.m. ¹	Pounds per acre ²	P.p.m.	Per cent extracted	P.p.m.	Per cent extracted
Acidity.....	988	2,125	30	96.96	925	7.31
Aluminum.....	60,500	121,000	33,400	44.79	49,800	17.67
Calcium.....	2,255	4,510	2,225	1.53	2,253	0.08
Iron.....	23,900	47,800	18,300	23.85	22,100	7.53
Magnesium.....	2,260	4,520	2,250	0.43	2,259	— ⁴
Manganese.....	420	840	400	4.76	415	1.19
Nitrate-nitrogen.....	13	26	29	22.69 ³	11	15.39
Nitrogen.....	1,450	2,900	1,451	— ⁴	1,450	— ⁴
Phosphorus.....	550	1,104	481	12.54	549	— ⁴
Potassium.....	12,560	25,130	40,140	28.95	12,420	1.11

Yellow gray silt loam

DETERMINED	ORIGINAL		EXTRACTED WITH KNO ₃		EXTRACTED WITH H ₂ O	
Dry matter.....	96.64 per cent		99.03 per cent		98.93 per cent	
	P.p.m.	Pounds per acre	P.p.m.	Per cent extracted	P.p.m.	Per cent extracted
Acidity.....	1,358	2,813	11	99.93	1,260	7.21
Aluminum.....	75,600	151,200	30,300	59.93	58,900	24.73
Calcium.....	1,960	3,920	1,950	0.51	1,958	— ⁴
Iron.....	20,100	40,300	16,700	14.44	19,600	2.48
Magnesium.....	2,095	4,180	2,090	— ⁴	2,090	— ⁴
Manganese.....	393	786	391	3.03	389	1.02
Nitrate-nitrogen.....	18	36	40	55.00 ³	15	16.66
Nitrogen.....	685	1,370	690	— ⁴	689	— ⁴
Phosphorus.....	336	693	275	18.15 ³	335	— ⁴
Potassium.....	17,900	35,800	24,100	25.72	17,880	0.11

Yellow silt loam

DETERMINED.....	ORIGINAL		EXTRACTED WITH KNO ₃		EXTRACTED WITH H ₂ O	
Dry matter.....	98.39 per cent		98.84 per cent		98.39 per cent	
	P.p.m.	Pounds per acre	P.p.m.	Per cent extracted	P.p.m.	Per cent extracted
Acidity.....	1,318	2,921	28	97.93	1,155	13.36
Aluminum.....	74,700	149,400	36,900	50.61	58,600	21.55
Calcium.....	3,425	7,850	3,400	0.72	3,410	0.43
Iron.....	37,100	74,200	2,930	21.01	33,900	8.62
Magnesium.....	2,665	5,330	2,660	— ⁴	2,664	— ⁴
Manganese.....	330	660	301	8.79	325	1.51
Nitrate-nitrogen.....	30	60	315	90.47 ³	23	23.33
Nitrogen.....	983	1,966	983	— ⁴	981	— ⁴
Phosphorus.....	346	691	292	15.61	339	2.02
Potassium.....	14,500	29,000	22,300	28.57 ³	14,400	0.69

¹ CaCO₃.

² Limestone requirements 2,000,000 pounds of soil.

³ Increase.

⁴ Within the limits of probable error.

While a considerable amount of a calcium is present in these soils, qualitative tests for carbonates showed only traces, which indicate that these soils are deficient in calcium carbonate. It may be added further that while these soils are well provided with potassium, the phosphorus and nitrogen contents are rather low. On the other hand, the aluminum content is very high.

Sweet clover (biennial variety) was the crop used in this work for the reason that it does not thrive in strongly acid soils, and will, therefore, respond more readily to soil treatment. Inoculated seeds were used in every case.

The experiments were carried out in 1-gallon pots, each holding about 5 kgm. (11 pounds) of soil.

Experiment I. Effect of aluminum salts, alone and in combination with calcium carbonate or with acid phosphate on sweet clover grown in sand

Three salts, aluminum sulfate, aluminum chloride and aluminum nitrate, and one hydroxide, aluminum monohydroxide, were used. When applied alone the chemicals were used in three different amounts, one, for the sake of convenience, is called normal application, the second, one-fifth the normal, and the third, five times the normal application. The basis for the normal application is the acidity or lime requirement of the yellow silt loam, which is 2921 pounds limestone per acre, or 6.79 gm. calcium carbonate per 5 kgm. of soil. In other words, the normal application is the chemical equivalent of the salts to 6.79 gm. of calcium carbonate. In combination with calcium carbonate or with acid phosphate the salts remained constant while calcium carbonate and acid phosphate were applied in three different amounts, normal, one-fifth normal and five times normal. The normal application of calcium carbonate is the lime requirement of the soil and that of acid phosphate the chemical equivalent to the normal application of the salts. For the sake of brevity, hereafter throughout the discussion, we will refer to these three different amounts as the normal, the minimum, and the maximum application.

The chemicals were thoroughly incorporated in the sand, and seeds of sweet clover were sown. In order to insure a sufficient number of good seedlings the seeds were sown rather freely, but as the plants grew they were gradually thinned out until finally only five plants were left in each pot. The plant-food solutions were prepared and applied as directed in Hopkins and Pettit's "Soil Fertility Laboratory Manual" (34). Two crops have been grown in this series. The first was planted on July 17 and harvested November 1, 1919; the second was planted on January 19, but because of some unknown causes the seedlings failed to attain a uniform stand, so the whole series was replanted on February 2. The crop was harvested on May 21. The yields for two crops are given in table 5.

During the first crop several things were observed which led up immediately to the setting up of another series; and to the introduction of some modifications in the treatment of the pots for the second crop. In the first place, it was noticed that on every pot receiving acid phosphate no plant would grow.

Since the application of acid phosphate was rather heavy, 964 pounds to the acre or 5.3 gm. per pot, it was thought that the failure of the plants to grow might have been due to excessive amounts of acid phosphate present rather than to the presence of aluminum; accordingly a new series with acid phosphate alone, and in combination with calcium carbonate, was set up. This was designated as 600 series. The results of this series are shown in plate 6. It proved the supposition true that acid phosphate in such amounts was injurious to seedlings. Even calcium carbonate in amounts sufficient to neutralize the acidity of the acid phosphate did not prevent the harmful effect of acid phosphate. With this experience the application of acid phosphate was reduced to from 100 to 400 pounds to the acre, in the second planting.

TABLE 5
Aluminum series (dry weight of five plants)

SERIES NUMBER	FIRST CROP ¹	SECOND CROP ³	SERIES NUMBER	FIRST CROP	SERIES NUMBER	FIRST CROP	SECOND CROP	SERIES NUMBER	FIRST CROP	SECOND CROP	SERIES NUMBER	FIRST CROP
	gm.	gm.		gm.		gm.	gm.		gm.	gm.		gm.
101	3.40 ²	9.73	201	4.10	301	3.50	8.89	401	9.13	11.11	411	8.51
102	0.00	3.60	202	0.00	302	0.00	1.85	402	8.74	14.07	412	10.42
103	2.85	8.20	203	0.00	303	1.40	8.02	403	10.80	12.29	413	0.00
104	0.00	0.00	204	0.00	304	0.00	0.00	404	3.67	12.14	414	7.14
105	16.59	13.06	205	17.15	305	11.99	11.68	405	15.41	13.24	415	9.16
106	1.65	5.50	206	0.80	306	4.22	5.38	406	13.13	11.38	416	14.87
107	18.52	10.04	207	16.07	307	16.17	19.73	407	9.36	9.74	417	14.03
108	0.00	2.72	208	0.00	308	0.00	2.55	408	0.00	10.56	418	0.00
109	0.85	2.02	209	0.00	309	4.00	1.93	409	20.00	11.68	419	9.72
110	0.00	4.07	210	0.00	310	0.00	6.56	410	0.00	14.50		

¹ Harvested at the age of 106 days.

² Average of 2 pots.

³ Harvested at the age of 108 days.

The second observation made was on the showing of the plants in the control pots of every series, except those of the aluminum monohydroxide series. The plants in these pots appeared to be suffering from lack of some elements. Since the plant-food solution applied to the pots did not contain calcium, it was thought that the plants in the controls might have been suffering from lack of calcium, in which case the results of the different treatments would not be comparable. Following this thought it was planned for the second crop to apply calcium silicate to each pot as a source of calcium, and in quantities having calcium equal to the amount contained in calcium carbonate applied as normal.

The third observation made was on the aluminum monohydroxide series in which all pots except those receiving the maximum amount of aluminum monohydroxide, and acid phosphate, show no effect of the presence of aluminum.

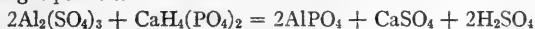
This compound, being insoluble, will produce no toxic effect, but it was thought that adding some substances which would yield acids on decomposition might change the aluminum hydroxide into a soluble form of aluminum, thus throwing further light on the form of aluminum compounds in the soil that produce toxicity. So it was planned for the next crop to introduce ammonium sulfate and dried blood in the series. Then the aluminum chloride series was dropped out in order to give way to this plan. Following is the plan of the experiments. Every treatment was carried out in duplicate.

PLAN OF THE EXPERIMENT

100 Series—Aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$

7.75 gm., or 3100 lbs. to the acre $\text{Al}_2(\text{SO}_4)_3 = 6.79 \text{ gm. CaCO}_3$

5.3 gm., or 964 lbs. to the acre $\text{CaH}_4(\text{PO}_4)_2 = 7.75 \text{ gm. Al}_2(\text{SO}_4)_3$ according to the following equation:



101. Control—Plant-food only

102. Plant-food + 7.75 gm. $\text{Al}_2(\text{SO}_4)_3$

103. Plant-food + $\frac{1}{5}$, or 1.55 gm. $\text{Al}_2(\text{SO}_4)_3$

104. Plant-food + $5 \times 7.75 \text{ gm.}$, or 38.75 gm. $\text{Al}_2(\text{SO}_4)_3$

105. Plant-food + 7.75 gm. $\text{Al}_2(\text{SO}_4)_3$ + 6.79 gm. CaCO_3

106. Plant-food + 7.75 gm. $\text{Al}_2(\text{SO}_4)_3$ + $\frac{1}{5}$, or 0.36 gm. CaCO_3

107. Plant-food + 7.75 gm. $\text{Al}_2(\text{SO}_4)_3$ + $5 \times$, or 33.95 gm. CaCO_3

108. Plant-food + 7.75 gm. $\text{Al}_2(\text{SO}_4)_3$ + 5.3 gm. $\text{CaH}_4(\text{PO}_4)_2$

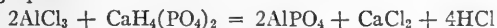
109. Plant-food + 7.75 gm. $\text{Al}_2(\text{SO}_4)_3$ + $\frac{1}{5}$, or 1.06 gm. $\text{CaH}_4(\text{PO}_4)_2$

110. Plant-food + 7.75 gm. $\text{Al}_2(\text{SO}_4)_3$ + $5 \times$, or 26.5 gm. $\text{CaH}_4(\text{PO}_4)_2$

200 Series—Aluminum chloride, AlCl_3

6.04, or 2405 pounds to the acre $\text{AlCl}_3 = 6.79 \text{ gm. CaCO}_3$

5.3 gm., or 964 pounds to the acre $\text{CaH}_4(\text{PO}_4)_2 = 6.04 \text{ gm. AlCl}_3$ according to the following equation:



201. Control—Plant-food only

202. Plant-food + 6.04 gm. AlCl_3

203. Plant-food + $\frac{1}{5}$, or 1.21 gm. AlCl_3

204. Plant-food + $5 \times$, or 30.2 gm. AlCl_3

205. Plant-food + 6.04 gm. AlCl_3 + 6.79 gm. CaCO_3

206. Plant-food + 6.04 gm. AlCl_3 + $\frac{1}{5}$, or 1.36 gm. CaCO_3

207. Plant-food + 6.04 gm. AlCl_3 + $5 \times$, or 33.95 gm. CaCO_3

208. Plant-food + 6.04 gm. AlCl_3 + 5.3 gm. $\text{CaH}_4(\text{PO}_4)_2$

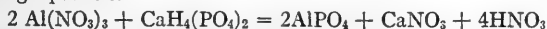
209. Plant-food + 6.04 gm. AlCl_3 + $\frac{1}{5}$, or 1.06 gm. $\text{CaH}_4(\text{PO}_4)_2$

210. Plant-food + 6.04 gm. AlCl_3 + $5 \times$, or 26.5 gm. $\text{CaH}_4(\text{PO}_4)_2$

300 Series—Aluminum nitrate, $\text{Al}(\text{NO}_3)_3$

9.65 gm., or 3859 pounds to the acre $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} \times 6.79 \text{ gm. CaCO}_3$

5.3 gm., or 964 pounds to the acre $\text{CaH}_4(\text{PO}_4)_2 = 9.65 \text{ gm. Al}(\text{NO}_3)_3$ according to the following equation:



301. Control—Plant-food only

302. Plant-food + 9.65 gm. $\text{Al}(\text{NO}_3)_3$

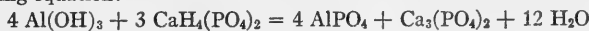
303. Plant-food + $\frac{1}{5}$, or 1.93 gm. $\text{Al}(\text{NO}_3)_3$

304. Plant-food + 5 X, or 46.25 gm. $\text{Al}(\text{NO}_3)_3$
305. Plant-food + 9.65 gm. $\text{Al}(\text{NO}_3)_3$ + 6.79 gm. CaCO_3
306. Plant-food + 9.65 gm. $\text{Al}(\text{NO}_3)_3$ + $\frac{1}{5}$, or 1.36 gm. CaCO_3
307. Plant-food + 9.65 gm. $\text{Al}(\text{NO}_3)_3$ + 5 X, or 33.95 gm. CaCO_3
308. Plant-food + 9.65 gm. $\text{Al}(\text{NO}_3)_3$ + 5.3 gm. $\text{CaH}_4(\text{PO}_4)_2$
309. Plant-food + 9.65 gm. $\text{Al}(\text{NO}_3)_3$ + $\frac{1}{5}$, or 1.06 gm. $\text{CaH}_4(\text{PO}_4)_2$
310. Plant-food + 9.65 gm. $\text{Al}(\text{NO}_3)_3$ + 5 X, or 26.5 gm. $\text{CaH}_4(\text{PO}_4)_2$

400 Series—Aluminum Hydroxide, $\text{Al}(\text{OH})_3$

3.5 gm., or 1399 pounds to the acre $\text{Al}(\text{OH})_3$ = 6.79 gm. CaCO_3

7.8 gm. $\text{CaH}_4(\text{PO}_4)_2$, or 1418.5 pounds per acre, or 3.5 gm. $\text{Al}(\text{OH})_3$ according to the following equation:



401. Control-Plant-food only
402. Plant-food + 3.5 gm. $\text{Al}(\text{OH})_3$
403. Plant-food + $\frac{1}{5}$, or 0.7 gm. $\text{Al}(\text{OH})_3$
404. Plant-food + 5 X, or 17.5 gm. $\text{Al}(\text{OH})_3$
405. Plant-food + 3.5 gm. $\text{Al}(\text{OH})_3$ + 6.79 gm. CaCO_3
406. Plant-food + 3.5 gm. $\text{Al}(\text{OH})_3$ + $\frac{1}{5}$, or 1.36 gm. CaCO_3
407. Plant-food + 3.5 gm. $\text{Al}(\text{OH})_3$ + 5 X, or 33.95 gm. CaCO_3
408. Plant-food + 3.5 gm. $\text{Al}(\text{OH})_3$ + 7.8 gm. $\text{CaH}_4(\text{PO}_4)_2$
409. Plant-food + 3.5 gm. $\text{Al}(\text{OH})_3$ + $\frac{1}{5}$, or 1.5 gm. $\text{CaH}_4(\text{PO}_4)_2$
410. Plant-food + 3.5 gm. $\text{Al}(\text{OH})_3$ + 5 X, or 39.0 gm. $\text{CaH}_4(\text{PO}_4)_2$

600 Series—Acid phosphate, $\text{CaH}_4(\text{PO}_4)_2$

601. Control—Plant-food only
602. Plant-food + 5.3 gm. $\text{CaH}_4(\text{PO}_4)_2$
603. Plant-food + $\frac{1}{5}$, or 1.06 gm. $\text{CaH}_4(\text{PO}_4)_2$
604. Plant-food + 5 X, or 26.5 gm. $\text{CaH}_4(\text{PO}_4)_2$
605. Plant-food + 5.3 gm. $\text{CaH}_4(\text{PO}_4)_2$ + 6.79 gm. CaCO_3
606. Plant-food + 5.3 gm. $\text{CaH}_4(\text{PO}_4)_2$ + $\frac{1}{5}$, or 1.36 gm. CaCO_3
607. Plant-food + 5.3 gm. $\text{CaH}_4(\text{PO}_4)_2$ + 5 X, or 33.95 gm. CaCO_3

PLAN FOR SECOND CROP

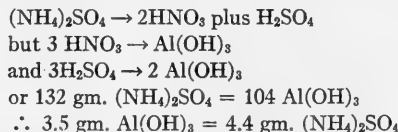
100 Series. The same as before with the addition of 7.9 gm. CaSiO_3 to each pot and the reduction of the acid phosphate application to from 100 to 400 pounds to the acre, or from 350 mgm. to 1.00 gm. per pot.

300 Series. The same plan as before with the same modification noted in the 100 series.

400 Series. Up to 410, inclusive, the same plan as before with the same modification as noted in the 100 series.

From 411 to 424 the following arrangement has been followed:

From 411 to 417, inclusive, 4.4 gm. $(\text{NH}_4)_2\text{SO}_4$ has been added according to the following reaction:



From 418 to 424, inclusive, 13.33 gm. of dried blood has been added, according to the following reaction. The dried blood used contained 14 per cent N, or 17 gm. NH_3 .

If all ammonia produced is nitrified, 2 HNO_3 is produced.

But $\text{HNO}_3 = \text{Al}(\text{OH})_3$

$\therefore 189 \text{ gm. HNO}_3 = 78 \text{ gm. Al}(\text{OH})_3$

3.5 gm. $\text{Al}(\text{OH})_3 = 8.4 \text{ gm. HNO}_3$, or 13.33 gm. dried blood

- 411. Plant-food + 3.5 gm. $\text{Al}(\text{OH})_3$ + 4.4 gm. $(\text{NH}_4)_2\text{SO}_4$ + 7.9 gm. CaSiO_3
- 412. Plant-food + 3.5 gm. $\text{Al}(\text{OH})_3$ + $\frac{1}{2}$, or 0.88 gm. $(\text{NH}_4)_2\text{SO}_4$ + 7.9 gm. CaSiO_3
- 413. Plant-food + 3.5 gm. $\text{Al}(\text{OH})_3$ + 5 \times , or 0.22 gm. $(\text{NH}_4)_2\text{SO}_4$ + 7.9 gm. CaSiO_3
- 414. Plant-food + 17.5 gm. $\text{Al}(\text{OH})_3$ + 4.4 gm. $(\text{NH}_4)_2\text{SO}_4$ + 7.9 gm. CaSiO_3
- 415. Plant-food + 3.5 gm. $\text{Al}(\text{OH})_3$ + 4.4 gm. $(\text{NH}_4)_2\text{SO}_4$ + 7.9 gm. CaSiO_3
- 416. Plant-food + 3.5 gm. $\text{Al}(\text{OH})_3$ + 4.4 gm. $(\text{NH}_4)_2\text{SO}_4$ + 7.9 gm. CaSiO_3
- 417. Plant-food + 3.5 gm. $\text{Al}(\text{OH})_3$ + 4.4 gm. $(\text{NH}_4)_2\text{SO}_4$ + 7.9 gm. CaSiO_3
- 418. Plant-food + 3.5 gm. $\text{Al}(\text{OH})_3$ + 13.33 gm. dried blood
- 419. Plant-food + 3.5 gm. $\text{Al}(\text{OH})_3$ + $\frac{1}{2}$, or 2.66 gm. dried blood
- 420. Plant-food + 3.5 gm. $\text{Al}(\text{OH})_3$ + 5 \times , or 66.65 gm. dried blood
- 421. Plant-food + 17.5 gm. $\text{Al}(\text{OH})_3$ + 13.33 gm. dried blood
- 422. Plant-food + 3.5 gm. $\text{Al}(\text{OH})_3$ + 13.33 gm. dried blood
- 423. Plant-food + 3.5 gm. $\text{Al}(\text{OH})_3$ + 13.33 gm. dried blood
- 424. Plant-food + 3.5 gm. $\text{Al}(\text{OH})_3$ + 13.33 gm. dried blood

Results and discussion. The effect of aluminum salts, of aluminum hydroxide and of acid phosphate on the growth of sweet clover, is best shown in the photographs in plates 2, 3, 4, 5 and 6.

In the first crop in which no compound as a source of calcium was applied to the pots, aluminum sulfate proved to be injurious to sweet clover even in very small amounts. This may be seen in pots 102, 103 and 104 in which aluminum sulfate alone was applied. In pot 104, which received the maximum application of the salt, absolutely no seed could germinate. Pot 106, receiving the normal application of aluminum sulfate and one-fifth the normal application of calcium carbonate, shows that in small amounts calcium carbonate cannot correct the toxic effect of aluminum. On the other hand, where calcium carbonate has been applied in larger amounts, normal and maximum, sweet clover exhibited enormous growth. In the case of pots receiving aluminum sulfate and acid phosphate, those receiving 964 pounds and 4820 pounds of acid phosphate per acre failed to grow any crop.

What has been said about the effect of aluminum sulfate on sweet clover can also be said for aluminum chloride and aluminum nitrate. But with aluminum hydroxide the result is different. The normal application of aluminum hydroxide did not have any effect on sweet clover; the maximum, however, caused some depression. It is also important to note that whereas in the combination of aluminum salts and the minimum acid phosphate application, no sweet clover grew, but in that of the aluminum hydroxide and minimum acid phosphate no effect was shown. This proves that the failure of sweet clover to grow in pots 109, 209 and 309 was due to the presence of aluminum rather than that of acid phosphate.

The results of the second cropping, in which calcium silicate was added as a source of calcium, and the application of acid phosphate has been reduced to from 100 to 400 pounds per acre, were different from those of the first crop.

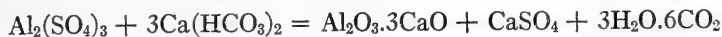
First, the normal application of aluminum sulfate did not show any toxic effect at all, while the maximum application was always fatal to sweet clover. Second, in every case where calcium carbonate was applied, no matter in what amount, good plants were growing, indicating that active aluminum has been put out of action. Acid phosphate in decreased amounts seemed to help in reducing the injurious effect of aluminum sulfate.

The results with aluminum nitrate were different from those noted in the case of sulfate. The normal application showed very toxic effects. While the maximum application of calcium carbonate was beneficial to clover the normal application did not entirely eliminate the toxicity of aluminum nitrate. The action of acid phosphate in eliminating the toxicity of aluminum nitrate was much less pronounced than in the case of the sulfate. From this difference of the behaviour of sweet clover on the two salts we are led to conclude that aluminum nitrate chemically equivalent to the acidity of the soil is more toxic than aluminum sulfate.

In the case of aluminum hydroxide, up to pot 419 with the exception of pots 413 and 419, the stand of sweet clover was uniform. Even the maximum application did not produce any effect on the growth of the plants. Pot 413 received 22 gm., the maximum application, of ammonium sulfate. The fact that sweet clover did not grow cannot be attributed to any cause but to an excessive amount of ammonium salt which, on breaking down, liberates ammonia that causes injury to the germinating seeds. Pot 418 received 13.33 gm., the normal application, of dried blood. Pot 419 received 2.66 gm., the minimum application, of dried blood. And the fact that on the former nothing grew, while on the latter the crop was as good as that in any other pot in the series, can be attributed also to the excessive amount of dried blood which on decomposition produces ammonia that hinders the germination of seeds. Apparently neither ammonium sulfate nor dried blood in smaller amounts was able to change aluminum hydroxide into other forms of aluminum which could produce the same effect as aluminum sulfate or nitrate.

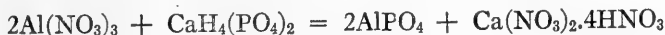
The effect of aluminum salts on sweet clover in the presence of calcium carbonate. In the series with aluminum sulfate, chloride and nitrate we have noted that in the presence of an excess of calcium carbonate the toxicity of the salts was overcome. Ruprecht and Morse (60) found this to be true also in their water-culture investigation with aluminum and iron sulfates in which, whenever calcium carbonate was added in excess to the solution containing aluminum and iron, the toxicity of these metals has been eliminated and good healthy plants grew in the solution. With this fact the question naturally arises as to what became of the aluminum. The most logical conclusion would be that aluminum had entered into combination with other elements forming an insoluble compound. Ruprecht and Morse (60) suggested that aluminum was precipitated as hydroxide and as such had no effect on the plants grown in the solution. The results of the test carried out in this work proved that aluminum monohydroxide has no effect on sweet clover. But whether the

hydroxide precipitated by the introduction of calcium carbonate is the variety that does not dissolve in water, acid and alkali, the author seriously doubts. In fact, he is of the opinion that the aluminum hydroxide precipitated by the introduction of calcium carbonate is like that formed when ammonia and sodium or potassium hydroxide is added to a solution containing aluminum. This is aluminum trihydroxide, which is insoluble in water and would therefore have no effect on the plants grown in solution. But this form of hydroxide is soluble even in dilute acids (53), and in sand or soil where chemical changes are constantly taking place this form of aluminum hydroxide will not remain long, for it will be converted into aluminum sulfate, chloride and nitrate as fast as free sulfuric, hydrochloric and nitric acids are produced in the soil and as long as the soil is not supplied with calcium or other suitable bases. For this reason the author looks into the formation of a more stable aluminum compound as an explanation for the elimination of active aluminum when calcium carbonate is added to sand or soil. He is of the opinion that as soon as calcium bicarbonate is formed by the action of carbonated water on calcium carbonate, the bicarbonate reacts with the aluminum salts forming calcium aluminate. The reaction may be written as follows:



Calcium aluminate is one of the constituents of portland cement and is a very stable compound. The formation of this compound seems to be the only satisfactory explanation for the ineffectiveness of aluminum as a toxic substance in the presence of sufficient calcium carbonate.

The effect of aluminum salts on sweet clover in the presence of acid phosphate. Mention has been made before that the 964 pounds per acre application of acid phosphate proved to be detrimental to sweet clover, and that the failure of the crop in the pots which received the normal and maximum application was brought about by the excess of acid phosphate. But in the second crop where the acid phosphate was applied in reduced amounts from 100 to 400 pounds per acre, the results showed that acid phosphate reduced the toxicity of aluminum. While the pots receiving the minimum and normal application in series 300 did not show any reduction of the toxicity of aluminum nitrate, the reduction of toxicity in the pot receiving 400 pounds of acid phosphate per acre is very pronounced, as indicated by the fairly good growth of the plants. Evidently the minimum and normal applications were not sufficient to convert the larger portion of aluminum into an insoluble form. Now the question arises as to how acid phosphate reduced the toxicity of aluminum. The answer is that with acid phosphate, aluminum sulfate, chloride and nitrate form an insoluble compound. In this case the compound is aluminum phosphate and is formed according to the following reaction:



Under soil conditions this reaction is probably never complete; nevertheless, a great amount of insoluble aluminum phosphate is formed. But the free nitric acid formed might also react with more aluminum, thus repeating the process until equilibrium is finally reached. Aluminum phosphate is highly insoluble and Wheeler (82) thinks that in the case of acid soils it is desirable to apply lime before or at the same time with acid phosphate in order to prevent formation of aluminum phosphate which is even more insoluble than tricalcium phosphate.

Experiment II. Effect of limestone and acid phosphate alone and in combination on the productivity and acidity of acid soils

Ten duplicate pots for each type of soil were filled with about 5 kgm. (11 pounds) of soil, and treated according to the following plan:

PLAN OF THE EXPERIMENT

700 Series—Gray silt loam

Acidity = 4.94 gm. CaCO_3 per 5 kgm., or 5.3 gm. limestone of 93 per cent purity, or 2125 pounds to the acre.

701. Control (nothing)
702. Soil + 5.3 gm. limestone
703. Soil + $\frac{1}{5}$, or 1.0 gm. limestone
704. Soil + 5 \times , or 26.5 gm. limestone
705. Soil + 5.8 gm. $\text{CaH}_4(\text{PO}_4)_2$ = 1.05 tons to the acre
706. Soil + $\frac{1}{5}$, or 1.16 gm. $\text{CaH}_4(\text{PO}_4)_2$ = 0.21 tons to the acre
707. Soil + 5 \times , or 29 gm. $\text{CaH}_4(\text{PO}_4)_2$ = 5.25 tons to the acre
708. Soil + 5.8 gm. $\text{CaH}_4(\text{PO}_4)_2$ = 5.3 gm. limestone
709. Soil + 5.8 gm. $\text{CaH}_4(\text{PO}_4)_2$ = $\frac{1}{5}$, or 1.06 gm. limestone
710. Soil + 5.8 gm. $\text{CaH}_4(\text{PO}_4)_2$ = 5 \times , or 26.5 gm. limestone

800 Series—Yellow gray silt loam

Acidity = 6.5 gm. CaCO_3 per 5 kgm., or 2813 pounds limestone to the acre

801. Control
802. Soil + 7.03 gm. limestone
803. Soil + $\frac{1}{5}$, or 1.40 gm. limestone
804. Soil + 5 \times , or 35.15 gm. limestone
805. Soil + 7.6 gm. $\text{CaH}_4(\text{PO}_4)_2$ = 1.4 tons to the acre
806. Soil + $\frac{1}{5}$, or 1.5 gm. $\text{CaH}_4(\text{PO}_4)_2$ = 0.28 tons to the acre
807. Soil + 5 \times , or 38.0 gm. $\text{CaH}_4(\text{PO}_4)_2$ = 6.00 tons to the acre
808. Soil + 7.6 gm. $\text{CaH}_4(\text{PO}_4)_2$ + 7.03 gm. limestone
809. Soil + 7.6 gm. $\text{CaH}_4(\text{PO}_4)_2$ + $\frac{1}{5}$, or 1.40 gm. limestone
810. Soil + 7.6 gm. $\text{CaH}_4(\text{PO}_4)_2$ + 5 \times , or 35.15 gm. limestone

900 Series—Yellow silt loam

Acidity + 6.79 gm. CaCO_3 per kgm., or 7.4 gm. limestone, or 2921 pounds limestone to the acre.

901. Control.
902. Soil + 7.3 gm. limestone
903. Soil + $\frac{1}{5}$, or 1.46 gm. limestone

904. Soil + 5 X, or 36.5 gm. limestone
 905. Soil + 7.6 gm. $\text{CaH}_4(\text{PO}_4)_2$, or 1.4 tons to the acre
 906. Soil + $\frac{1}{2}$, or 1.58 gm. $\text{CaH}_4(\text{PO}_4)_2$, or 0.28 tons to the acre
 907. Soil + 5 X, or 39 gm. $\text{CaH}_4(\text{PO}_4)_2$, or 6.00 tons to the acre
 908. Soil + 7.8 gm. $\text{CaH}_4(\text{PO}_4)_2$ + 7.3 gm. limestone
 909. Soil + 7.8 gm. $\text{CaH}_4(\text{PO}_4)_2$ + $\frac{1}{2}$, or 1.46 gm. limestone
 910. Soil + 7.8 gm. $\text{CaH}_4(\text{PO}_4)_2$ + 5 X, or 36.5 gm. limestone

Two crops have been harvested in these series. The first was planted on August 22, 1919, and harvested November 30, 1919, a period of only 100 days. The time of cropping could have been prolonged, but when the crop was moved into the greenhouse, the red spider infested it so badly that it was thought best to cut the crop down in order to eradicate the red spider at once. The second crop was planted on January 16, 1920, and harvested May 21, 1920, after a period of 125 days. The yield of the crops is given in table 6.

TABLE 6
Soil series (dry weight of five plants)

GRAY SILT			YELLOW GRAY SILT			YELLOW SILT		
Series number	First crop ¹	Second crop ³	Series number	First crop	Second crop	Series number	First crop	Second crop
	gm.	gm.		gm.	gm.		gm.	gm.
701	0.54 ²	2.02	801	0.27	0.40	901	0.52	0.79
702	0.81	2.77	802	0.68	2.29	902	0.64	1.26
703	0.70	2.07	803	0.26	0.26	903	0.52	1.29
704	1.28	5.35	804	0.97	3.45	904	1.41	2.11
705	0.87	2.20	805	0.40	0.60	905	0.75	4.72
706	0.58	1.62	806	0.23	1.68	906	0.62	1.38
707	1.12	3.18	807	0.67	1.48	907	1.21	1.45
708	1.65	5.88	808	0.71	10.58	908	1.19	4.67
709	0.76	1.58	809	0.34	1.80	909	0.71	1.10
710	1.43	7.42	810	1.45	14.67	910	1.66	6.49

¹ Harvested at the age of 106 days.

² Average of 2 pots.

³ Harvested at the age of 108 days.

For each type of soil a corresponding set of treated pots was laid aside, without plants for acidity determination. Two determinations were made, the first on December 8, 1919, after a lapse of 108 days from the time the pots were set aside, and the second on February 16, 1920, a period of 70 days after the first determination. Table 7 shows the results of these determinations.

Results and discussion. The effect of lime and acid phosphate on sweet clover grown on acid soils can best be seen in the photographs in plates 6, 7, and 8. It can be seen that all the three types of soil respond to liming. The normal and maximum applications especially brought excellent results. The plants were healthy, vigorous and dark green. Limestone applied in amounts equal to one-fifth of the lime requirement did not benefit the soil at all. The growth of the plants in this case was comparable to that of the control in which

TABLE 7

Acidity determinations of treated soils

SERIES NUMBER	SAMPLED DECEMBER 8, 1919				SAMPLED FEBRUARY 16, 1920				
	P.p.m.	Acidity reduced after 108 days	Acidity above or below control	Acidity reduced due to treatment	P.p.m.	Acidity reduced after 178 days	Acidity above or below control	Acidity reduced between dates of sampling	Acidity reduced due to treatment

Gray silt loam. Original acidity—988 parts per million, or 2125 pounds of limestone per acre

		per cent	per cent	per cent		per cent	per cent	per cent	per cent
701	705	28.66			685	30.87		2.83	
702	165	83.29	76.59	54.63	74	92.51	89.19	55.15	62.64
703	640	35.22	9.22	6.56	425	56.98	37.95	33.59	26.11
704	26	97.26	96.31	68.60	Alkaline	100.00	0.00	0.00	
705	545	44.83	22.69	16.17	217	78.03	68.32	41.83	47.16
706	810	18.01	12.96		687	30.46	0.29	15.18	
707	467	52.85	33.75	24.19	115	88.35	83.19	75.37	57.48
708	106	89.27	84.96	60.61	Alkaline	100.00	0.00	0.00	
709	437	56.78	38.96	21.12	243	75.40	64.52	44.39	44.53
710	20	97.97	96.32	69.31	Alkaline	100.00	0.00	0.00	

Yellow gray silt loam. Original acidity—1358 parts per million, or 2813 pounds of limestone per acre

801	1066	21.63			970	28.57		9.00	
802	42	96.90	96.06	75.27	Alkaline	100.00	0.00	0.00	
803	542	60.09	49.06	38.46	362	73.34	61.64	33.21	44.7
804	Alkaline	100.00	0.00		Alkaline	0.00	0.00	0.00	
805	764	43.00	28.33	21.37	580	57.29	40.20	24.08	28.62
806	895	33.28	16.04	11.65	894	34.16	7.83	0.11	5.59
807	479	63.91	55.09	42.28	271	80.04	72.06	41.33	51.47
808	110	91.91	90.62	70.28	Alkaline	100.00	0.00	0.00	
809	565	65.75	46.43	44.12	519	61.78	46.49	8.01	33.21
810	Alkaline	100.00	0.00	0.00	Alkaline	100.00	0.00	0.00	

Yellow silt loam. Original acidity—1318 parts per million, or 2921 pounds of limestone per acre

901	685	48.02			683	48.18		0.29	
902	77	94.16	88.76	46.13	13	99.01	98.09	83.11	50.83
903	511	61.22	25.40	13.20	243	81.56	64.42	52.44	33.38
904	Alkaline	0.00	0.00		Alkaline	0.00	0.00	0.00	
905	630	52.20	8.26	4.18	441	65.78	35.43	30.00	17.60
906	832	36.71	17.66		645	51.06	5.56	22.47	2.88
907	455	65.47	33.57	17.45	123	90.66	81.99	72.96	52.48
908	109	91.72	84.09	43.70	Alkaline	100.00	0.00	0.00	0.00
909	846	35.81	19.05		642	51.29	6.00	24.11	3.11
910	16	98.78	96.21	50.76	Alkaline	100.00	0.00	0.00	

the plants were very small and chlorotic. The results with acid phosphate applied alone, showed that the soils also respond to phosphate fertilization. Judging from the growth of the plants even the minimum application seems to have benefited the soil. In the first crop, however, the plants looked different from those growing on limed pots. The plants grew more than those in the control, but they were slender, branchless, and chlorotic as compared with the bushy dark green plants growing on the limed pots. In the second crop, excepting the crops in the pots which received the minimum application, those defects observed above have disappeared, and although growth was slow during the winter days, the plants were healthy, bushy and deep green. The best crop in this series was noted in the pots receiving the normal application and maximum application of limestone, together with the normal application of acid phosphate. Even the minimum application of limestone in combination with the normal amount of acid phosphate grew better crops than the normal application of limestone alone. In the first crop, however, the plants were also chlorotic, although to a lesser extent than those in pots receiving acid phosphate alone. In the second crop chlorosis has completely disappeared.

After the first acidity determination it was found that the acidity of the untreated soil has been reduced also. The acidity of the gray silt loam has been reduced 28 per cent, that of the yellow gray silt $21\frac{1}{2}$ per cent and that of the yellow silt 48 per cent. Up to this time, for a period of 108 days, tap-water was used for watering the plants and the pots, but since then rain-water was used instead. Experience in the use of this tap-water in the greenhouse proved that it has a tendency to reduce the acidity of acid soils. For example, a very acid soil watered by the tap-water became alkaline after a few years. The fact that the acidity of the controls of the three types of soil have been reduced is attributed to the use of the tap-water. But by subtracting the per cent of acidity reduced in the control from the total acidity of the treated pots, we still have a fair indication of the acidity reduced due to the treatment of the soils.

The effect of limestone and acid phosphate alone and in combination on the acidity of the three acid soils is best shown in plates 11 and 12, in which the treatment of the pots is represented by the abscissas and the per cent of acidity reduced by the ordinates. Curve 1 in each figure represents the per cent of acidity reduced after 108 days and curve 2 the total acidity reduced for a period of 178 days.

The three types of soil responded differently to the different treatments. Of the three the yellow gray silt loam responded more readily to liming and phosphate fertilization than either of the other two types. From the charts we can see that in 108 days the normal application of limestone or the amount required to neutralize the acidity of the soil reduced the acidity of the gray silt about 55 per cent, of the yellow silt 46 per cent and that of the yellow gray silt 76 per cent. In 178 days the total acidity reduced was 63 per cent for the gray silt and 51 per cent for the yellow silt; the yellow gray silt was com-

pletely neutralized, the reaction being alkaline. With one-fifth of the normal application the acidity was reduced 6.56 per cent in the case of gray silt, in 108 days; 38 per cent in case of the yellow gray, and 13 per cent in case of the yellow silt. At the end of 178 days the lime applied was completely used up in the neutralization of one-fifth of the acidity of the soil. In the case of the yellow gray silt the percentage of acidity reduced in both determinations exceeds that which would theoretically be accomplished by lime applied in an amount equal to one-fifth of the lime requirement. This fact is probably due to experimental error which would include sampling and manipulation. When limestone equal to five times the lime requirement was added, the neutralization of acidity was complete in 108 days in the case of two soils; only 68.8 per cent of the acidity was reduced in the case of gray silt. All these facts indicate the rapidity with which calcium carbonate puts active aluminum out of action, the substance responsible for the acidity of the soils.

The effect of acid phosphate on the three soils is interesting. The notion that acid phosphate has the tendency to increase the acidity of a soil has no confirmation in this work. On the contrary, the results show that acid phosphate decidedly reduced the acidity of the soil, as measured by the Hopkins method. The reaction, however, is slower than that in the case of calcium carbonate. In 108 days the normal application of acid phosphate destroyed 16 per cent of the acidity of the gray silt; 21 per cent of that of the yellow gray silt; and 4 per cent of that of the yellow silt. At the end of 178 days 47 per cent of the acidity of the gray silt was destroyed; 28 per cent of that of the yellow gray silt and only 17 per cent of that of the yellow silt. Applied in one-fifth the normal application, acid phosphate reduced in 178 days the acidity of the gray silt 7 per cent; of the yellow gray silt 12 per cent; and of the yellow silt only 3 per cent. In five times the normal application acid phosphate reduced the acidity of the gray silt 24 per cent in 108 days and 57 per cent in 178 days; of the yellow gray silt 42 per cent in 108 days and 51 per cent in 178 days; of the yellow silt 17 per cent in 108 days and 52 per cent in 178 days.

The combination of acid phosphate and limestone produced a still more interesting result. The combination of the normal application of limestone and acid phosphate reduced, in 108 days the acidity of the gray silt 60 per cent; of the yellow gray silt 70 per cent; and of the yellow silt 43 per cent. After 178 days all the pots with this treatment were alkaline. The combination of the normal application of acid phosphate and one-fifth the normal dose of limestone also reduced considerably the acidity of the soils. But with the combination of the normal application of acid phosphate and the maximum of limestone, the yellow gray silt was alkaline in 108 days, while the gray and yellow silt were then reduced 69.31 per cent and 50.76 per cent, respectively. At the end of 178 days the soils were alkaline.

How acid phosphate reduces the acidity of acid soils. One of the problems in the present investigation is whether acid phosphate increases the acidity of an acid soil. Using the calcium-acetate method Hartwell and Pember (27) found

that the acidity of acid soils increases as the amount of acid phosphate applied was increased. Comparing the lime-water and the potassium-nitrate methods Albrecht¹ found also that with the lime-water method the acidity increased as the amount of acid phosphate was increased, but with the potassium-nitrate method up to a certain point, the increase of acid phosphate was accompanied by a decrease of acidity. The results discussed in the preceding paragraph corroborate the findings of Albrecht with the potassium-nitrate method. In this connection two questions come up. First, if acid phosphate reduced the acidity of the soil, how? And second, why are the results between the potassium-nitrate method on the one hand, and those of calcium-acetate and lime-water on the other, so diametrically opposed?

Hartwell and Pember (27) noted that while the acidity of the soils was increased with the increase of acid phosphate application the amount of active aluminum was decreased. No explanation was offered for this fact, but we can safely attribute it to the combination of active aluminum with other elements forming an insoluble compound. One of the products of the reaction between acid phosphate and active aluminum in the soil is aluminum phosphate, a very insoluble compound. The decrease in the amount of active aluminum after acid phosphate has been applied to the soil is, therefore, due to the formation of aluminum phosphate. The larger the amount of acid phosphate applied to the soil containing active aluminum, the larger will be the amount of aluminum phosphate formed. And since aluminum is largely responsible for the acid reaction of the potassium nitrate extract, the larger the amount of aluminum converted into phosphate, the smaller will be the amount of aluminum that will be brought into solution when an acid soil is extracted with potassium nitrate after acid phosphate has been applied. This explains the fact that with the potassium-nitrate method the acidity of acid soils decreases as the amount of acid phosphate applied increases.

We can see from the above explanation that the opposing results obtained by the use of the three methods of determining the acidity of the soil are due to the difference of the substances determined. The lime-water and calcium-acetate methods determine true acidity, and the potassium-nitrate method, while originally intended to determine true acidity, actually determines active aluminum. Since acid phosphate has some free phosphoric acid the first two methods will record increased acidity as the amount of acid phosphate is increased.

Hartwell and Pember (27) also observed that in spite of the large amount of acidity (as determined by calcium acetate) due to acid phosphate, barley made a marked growth. In the present investigation the growth of sweet clover on pots receiving acid phosphate alone increased as the acid phosphate applied increased. But the correlation is between growth and decrease of acidity rather than growth and increase of acid phosphate. This is better

¹ W. Albert Albrecht's unpublished work in the University of Illinois.

illustrated in table 8 in which the per cent of acidity reduced and the dry matter of five plants from each pot are put together.

The results given are one of the evidences that aluminum is an important factor in the acidity of the three types of soil studied.

TABLE 8

Effect of the reduction of acidity by acid phosphate on the yield of sweet clover
Gray silt

Pot number.....	701	705	706	707
Per cent of acidity reduced.....		16.16	5.70	24.19
Dry weight (gm.).....	0.54	0.87	0.58	1.12

Yellow gray silt

Pot number.....	801	805	806	807
Per cent of acidity reduced.....		21.37	11.65	42.28
Dry weight (gm.).....	0.27	0.40	0.23	0.67

Yellow slit

Pot number.....	901	905	906	907
Per cent of acidity reduced.....		4.18	1.36	17.45
Dry weight (gm.).....	0.52	0.75	0.62	1.21

Experiment III. What happens when acid soils are leached out with potassium nitrate or water

Two pots of each of the three types of soil were leached out with normal potassium nitrate until the last 125 cc. of leachings were practically neutral. With the gray silt loam 30 liters of the solution per pot were needed to reach this point. For the yellow gray silt loam 35 liters were needed, and for the yellow silt 39 liters. After leaching with potassium nitrate the soil was leached out with distilled water again in order to get rid of the excess of potassium nitrate. The leaching was continued also until the last few drops showed faintly blue to the diphenylamine sulfuric acid test for nitrates. Then the soils were dried out and sampled for analysis. The results of the analysis are given in column 3, table 4.

A similar set was leached out with water alone. Distilled water was used in leaching the soils and the operation was continued until the last 125 cc. needed hardly 0.5 cc. of the standard sodium hydroxide solution used in titrating the acidity. When this end was reached, 12 liters of water had been used in the gray silt; 16 liters in the yellow gray silt; and 13 liters in the yellow silt. Then the soil was dried and sampled as in the above set for analysis. The results of the analysis are given in column 5, table 4.

What has been found from the above experiments may be summarized as follows. With potassium nitrate 96.96 per cent of the acidity of the gray silt

was extracted, with water only 7.31 per cent of the acidity was extracted. Of the aluminum 44.79 per cent was leached out by potassium nitrate and 17.67 per cent by water; of the iron 23.85 per cent was leached out by potassium nitrate and 7.53 per cent by water; of the manganese 4.76 per cent and 1.19 per cent were leached out by potassium nitrate and water, respectively. Potassium increased 28.95 per cent and nitrate nitrogen 20.69 per cent.

With the yellow gray silt 99.15 per cent of the acidity was extracted by potassium nitrate and 7.21 per cent by water; 59.93 per cent of the aluminum was leached out by potassium nitrate and 24.73 per cent by water; 14.44 per cent of the iron was leached out by potassium nitrate and 2.48 per cent by water; and of manganese 3.03 per cent and 1.03 per cent was leached out by potassium nitrate and water, respectively. Potassium was increased 25.72 per cent and nitrate nitrogen 55.60 per cent.

With the yellow silt, potassium nitrate extracted 97.93 per cent of the acidity, and water 12.36 per cent; of aluminum 50.61 per cent was leached out by potassium nitrate and 21.55 per cent by water; of iron 21.01 per cent was leached out by potassium nitrate and 8.62 per cent by water; of manganese 8.79 per cent was extracted by potassium nitrate and 1.51 per cent by water. Potassium was increased by 28.57 per cent and nitrate nitrogen by 90.47 per cent. It may be added that potassium nitrate also leached out some of the calcium and phosphorus of the soils.

Discussion of results. These results reveal the fact that from 44 to 60 per cent of the aluminum in the soil may be leached out by potassium nitrate and that the leaching of this amount is accompanied by a big decrease in the acidity. Thus the 44.79 per cent of aluminum leached out from the gray silt was accompanied by the disappearance of 96.96 per cent of the acidity. In the case of the yellow gray silt the extraction of 59.93 per cent was accompanied by the destruction of 99.15 per cent of the acidity. With the yellow silt 50.61 per cent of the aluminum extracted was equivalent to a 97.93 per cent decrease in the acidity. It is not to be expected to extract all the aluminum in order to reduce the acidity of the soil to zero, for not all the aluminum in the soil is in the form readily soluble in potassium-nitrate solution. Some of the aluminum is present as silicate and since clay constitutes from 10.15 to 26.4 per cent of the bulk of the soils under experiment, it is not unlikely that kaolinite, $\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5$, the chief constituent of clay, is present in considerable amounts. Kaolinite is a very stable compound, and although kaolin (70), a mechanical mixture of kaolinite and silica, has been found to exchange bases with salt solutions, nevertheless, under the conditions in which the aluminum has been leached out in the present work, it is not probable that kaolinite and allied aluminum minerals will be readily attacked by potassium nitrate solutions. The case is more likely to be that a considerable amount of soluble aluminum compounds—salts and the trihydroxides—are present in the soil. In contact with potassium nitrate or even with water these compounds readily go into solution and are leached out. The 40 or 60 per cent of aluminum

leached out represents these soluble compounds or active aluminum. This active aluminum is equivalent approximately to 53,240 and 90,720 pounds per acre, respectively.

In the case of the water-leached soils it is seen that from 17.67 per cent to 24.73 per cent of the aluminum is leached out. These percentages are equivalent approximately to 20,570 pounds and 26,388 pounds per acre, respectively. The quantity of aluminum found in the water leachings would not probably be the actual amount of soluble aluminum in the field because certain factors, such as the transporting, storing and drying of the soil when brought to the greenhouse, might have contributed to the increase of the solubility of aluminum, but allowing 50 per cent to these factors we have still about 10,000 or 18,000 pounds left to be assigned to the readily soluble aluminum in the soils. The amount of aluminum in the maximum application of aluminum nitrate in the sand series is equivalent to 2701 pounds only, and this proved fatal to sweet clover. In the normal application of the same salt the aluminum is equivalent to 540 pounds per acre only, yet this proved toxic to sweet clover. If this is true what a tremendous influence will 10,000 or 18,000 pounds have on the crop in the field.

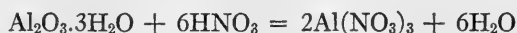
Sweet clover on the leached-out soils. Sweet clover seeds were sown in both potassium-nitrate-leached and water-leached soils. In the case of the former there were some difficulties which were never overcome in the case of two soils up to the writing up of this work. First, too much potassium nitrate was left in the soils in spite of the leaching by water. Gray silt loam had 28.69 per cent more nitrate nitrogen and 28.95 per cent more potassium than the original. Yellow gray silt loam had 55 per cent more nitrate nitrogen, and 25.72 per cent more potassium than the original; and the yellow silt had 90.27 per cent more nitrate nitrogen and 28.57 per cent more potassium. The second difficulty was the physical texture of the soils which was badly affected by the leaching with potassium nitrate. The soils became more compact and sticky. The first planting was consequently a failure. An attempt has been made to improve the physical texture of the soil by mixing the soil with one-third of its volume of pure silica sand and leaching out with water again. But the nitrate remaining was still in large enough amounts to be fatal to seedlings, consequently the second planting was again a failure. The soils were laid aside and watered every day until it was thought enough nitrate salt had been drained out. Seeds were then planted. At the beginning the seedlings seemed to be making headway, but within three weeks the seedlings in the yellow gray and yellow silt loams were already either dead or dying. Evidently the concentration of salts in these two types of soil was still too strong for the plants to survive. In the case of the gray silt the seedlings persisted and grew, although slowly. The growth up to May 19, at the age of 120 days, is shown in plate 9. A, is water-leached soil, A-1 is potassium-nitrate-leached soil, A-2 original soil plus KNO_3 equivalent to the excess found in the KNO_3 -leached soil plus sand, A-3, the original soil plus sand. Attention

is called to the difference of the growth of sweet clover on the different pots. The plants in the potassium-nitrate-leached soil, although somewhat stunted in growth, were really healthy and deep green. The plants in A-2 and A-3 were largely chlorotic. This difference in the growth is attributed to the reduction of 96 per cent of the acidity of the soil, which is equivalent to 53,240 pounds of aluminum removed. It is also important to note the growth of sweet clover on the water-leached soil. Although only 96 days old they looked just as vigorous as those in the potassium-nitrate-leached soil. This was due chiefly to the presence of a still excessive amount of the nitrate salt in the potassium-nitrate-leached soil. But it is evident that the removal of about 20,000 pounds of aluminum by water had greatly benefited the growth of sweet clover and this amount was probably the amount of active aluminum immediately concerned in the unproductivity of the soils under investigation. This effect of the removal of about 44 per cent of aluminum in the soil by potassium nitrate and 17 per cent by water, on the growth of sweet clover, is conclusive proof that aluminum is the chief factor in the unproductivity of the three types of soil under investigation and probably of most acid soils in America.

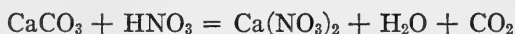
How aluminum salts arise in the soil. The form of aluminum immediately concerned in the behaviour of sweet clover toward acid soils is the soluble form, the salts. The silicates and hydroxides cannot produce toxicity inasmuch as they are insoluble in water. In the case of one form of hydroxide, the monohydroxide, it has been proven harmless to sweet clover in the present investigation. But the salts have been proven injurious to plants even in dilute solutions.

The question now arises as to how aluminum salts may be formed in the soil. Aluminum chloride, sulfate and nitrate may all be found in the soil. The amount of aluminum chloride will naturally be limited by the absolute amount of chlorine in the soil. Aluminum sulfate will also be limited by the amount of sulfur. Under certain conditions, if the soil is rich in sulfur and the sulfur bacteria are active, through sulfofication considerable amounts of aluminum sulfate may be formed. Investigating the effect of sulfofication on the availability of potassium in the soil, Ames and Boltz (2) found that aluminum was not present in the extract of soils in which sulfur did not enter as a part of the treatment, and concluded that aluminum sulfate is formed during sulfofication. Artificial treatment of the soil may give rise to considerable amounts of aluminum sulfate. Ruprecht and Morse (60) found that the continuous application of ammonium sulfate to plots in the experimental field in Massachusetts produced aluminum sulfate. But great as is the possibility of the formation of aluminum sulfate in large quantities, still greater is the possibility for the formation of aluminum nitrate. Nitrification is a normal process occurring in the soil, and depending on conditions it varies widely. At certain seasons of the year nitrification is most active. Such is the condition under which large quantities of aluminum nitrate may be formed. In

normal soils, sufficiently provided with limestone, aluminum salt may never be formed, but in soils deficient in limestone, aluminum salts are largely formed; especially is it true when nitrification is most active. The acid-soluble aluminum trihydroxide in the soil, in the absence of limestone and other suitable bases, unites with nitric acid forming aluminum nitrate. The reaction may be represented by the following equation:



If limestone is present in sufficient quantities to satisfy the basic need of nitric acid produced, aluminum nitrate and sulfate may never be formed. Calcium nitrate, the best form of nitrogen compound for plant-food is formed, instead, according to the following reaction:

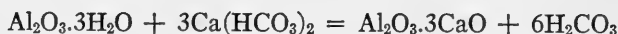


Ames and Boltz (2) noted that the largest amount of aluminum was found in solutions from soils where sulfur was oxidized in the absence of calcium carbonate.

What happens when acid soils are extracted with potassium nitrate before and after the application of limestone. The fact has been repeatedly observed in the present investigation that when an acid soil was extracted with potassium nitrate the reaction of the extract was always acid, but when limestone (calcium carbonate) was applied in amounts equivalent to or five times the lime requirement, and the soil was extracted with potassium nitrate the reaction of the extract was always alkaline and the white gelatinous aluminum hydroxide precipitate was absent. Knight² found that "when a base is added to an acid soil, comparatively insoluble products are formed. Calcium produces a product less soluble than does potassium." Ames and Boltz (2) also found that the addition of calcium carbonate at the rate of 80,000 parts per million on the soil, decreased the solubility of aluminum to 68 parts per million as compared with 660 parts per million where calcium was added in amounts just sufficient to combine with only a small part of the sulfuric acid. What most probably happens is this: When calcium carbonate is applied to the soil, calcium bicarbonate is formed which unites with the aluminum salts or with the acid-soluble hydroxide, forming calcium aluminate, a stable compound. The reaction may be written as follows:



or



When an acid soil comes in contact with potassium nitrate solution an exchange of bases between the soil and the solution takes place (70). The

² H. G. Knight, "Acidity and Acidimetry of Soil," unpublished thesis from the University of Illinois.

aluminum compounds are attacked, bringing aluminum into solution and forming aluminum nitrate which on hydrolysis produces strong acidity. This is the cause of the acid reaction of the solution. When an acid soil is treated with calcium carbonate and after a while extracted with potassium nitrate the extract is alkaline. An exchange of bases takes place also. But in this case the calcium compounds formed in the soil are attacked by the salt solution, calcium being replaced by potassium and brought into solution as calcium nitrate. Such an explanation is in agreement with the findings of van Bemmelen (5) and other investigators (70) on the subject of exchange of bases between soils and salt solutions, the former having found that when potassium chloride solution was added to the soil, almost a complete change of potassium for calcium and magnesium took place. The presence of calcium nitrate, therefore, which does not hydrolyze, explains the neutral or alkaline reaction of the extract.

Experiment IV. Iron and manganese as factors in soil acidity

The table of analysis reveals that the types of soil under investigation also contain considerable quantities of iron and manganese. The gray silt contains 47,800 pounds of iron and 840 pounds of manganese per acre. The yellow gray silt contains 40,300 pounds of iron and 786 pounds of manganese per acre; and the yellow silt contains 74,200 pounds of iron and 660 pounds of manganese per acre. The toxicity of normal iron salts at a certain concentration is well known, and Ruprecht and Morse (61) found that in the unproductivity of ammonium-sulfate fertilized plots of the Massachusetts Agricultural Experiment Station, ferric and manganese salts were also contributing factors. Funchess (20) also observed that in Alabama the development of soluble manganese salts was the cause of the unproductivity of a certain soil. The question now comes up as to whether iron and manganese might not be also contributing factors in the acidity of the soils under investigation. It was thought that if these metals were as important a factor as aluminum, some idea might be obtained from their degree of solubility and their ratio to soluble aluminum. Fortunately, the first 4-liter potassium-nitrate leachings of the gray silt and the first 4-liter water-leachings of the three types of soil have been saved. These leachings were analyzed for aluminum, iron and manganese. The results of the analysis are given in table 9.

This table shows that the ratio of aluminum, iron and manganese in the first 4 liters of the potassium-nitrate leachings is 4.6:1:1.2. The first 4 liters of water extract gave for the gray silt loam 4.8 for aluminum, 1 for iron and 1.1 for manganese; for the yellow gray silt loam 6.2 for aluminum, 1 for iron and 1.3 for manganese; and for the yellow silt 3.4 for aluminum, 1 for iron and 1.7 for manganese. The proportion of aluminum to iron or manganese is such that there can be no doubt that aluminum is the dominant factor. In the case of manganese a further step has been taken. Sand-culture experiments were

carried out with manganese sulfate, nitrate and carbonate, the plan being the same as that in the aluminum series. The results of these experiments reveal that manganese cannot be any factor in the soil in question for this reason. When calcium carbonate in considerable quantities was combined with aluminum salts the toxicity of the aluminum was corrected. In the case of the soils, calcium carbonate also corrected their acidity or unproductivity, but with manganese compounds not even the application of five times the lime requirement of calcium carbonate has corrected the toxicity of manganese. It is not denied that iron and manganese might become factors in the acidity of some soils but with the soils under investigation there is no doubt that aluminum is the determining factor in their acidity.

TABLE 9
Analysis of extracts (4 liters)

TYPE OF SOIL	DETERMINED		
	Aluminum	Iron	Manganese
	KNO ₃ extract		
Gray silt (mgm.).....	282.5	60.9	49.8
Ratio.....	4.6	1	1.2
	H ₂ O extract		
	Aluminum	Iron	Manganese
	KNO ₃ extract		
Gray silt (mgm.).....	75.5	15.8	14.6
Ratio.....	4.8	1	1.1
Yellow gray silt (mgm.).....	105.2	17.0	13.1
Ratio.....	6.2	1	1.3
Yellow silt (mgm.).....	88.9	26.3	16.3
Ratio.....	3.4	1	1.7

V. SUMMARY

Experiments have been carried out, first, to find out the influence of aluminum salts and aluminum hydroxide, alone and in combination with calcium carbonate or with acid phosphate, on the growth of sweet clover grown in sand; second, to determine the effect of limestone and acid phosphate alone and in combination, on the productivity and acidity of three types of silt loam soil; third, to find out the effect of the removal of some aluminum from the soil on the growth of sweet clover; and fourth, to ascertain whether iron and manganese also are factors in the acidity of the soils under investigation.

In the absence of some calcium compounds as a source of calcium, aluminum salts were highly toxic to sweet clover when applied in amounts chemically equivalent to the acidity of the soil, and fatal to sweet clover when applied in

amounts chemically equivalent to five times the acidity of the soil. In the presence of calcium silicate, aluminum nitrate was more toxic than aluminum sulfate.

Aluminum mono-hydroxide had no effect whatever on the growth of sweet clover, when other plant-food elements were added in water-soluble form.

Calcium carbonate in sufficient amounts corrected the toxicity of aluminum salts, by precipitating aluminum as calcium aluminate, an insoluble compound.

Acid phosphate applied at the rate of 400 pounds per acre reduced the toxicity of aluminum salts by forming aluminum phosphate, an insoluble aluminum compound.

Limestone applied at a rate equal to the lime requirement produced good crops on the three silt loam soils; applied at the rate of five times the lime requirement it produced better crops. At the same rate of application the soils were alkaline at the end of 178 days. The action of calcium carbonate in the soil is to unite with the aluminum salts and the acid-soluble aluminum hydroxide, forming calcium aluminate.

Acid phosphate applied alone at the rate of 1 ton to the acre produced fair crops, at the rate of 5 tons good crops. Acid phosphate also reduced the acidity of the soils and the decreases depended on the rate of application. At the rate of 5 tons per acre acid phosphate reduced the acidity of the soils from 51 to 57 per cent. The reduction of the acidity was due to the formation of the insoluble aluminum phosphate.

The combination of acid phosphate and limestone in large quantities produced the best crops.

The aluminum in the soil varies from 121,000 to 151,000 pounds per acre. When the soil was leached out with potassium nitrate solution until the last 125 cc. of leachings was practically neutral, the acidity of the soil was reduced 99 per cent and as much as 59 per cent of the aluminum was leached out. Sweet clover growing on leached soil was better than that growing on unleached soil. The fact conclusively proved that aluminum is the determining factor in the acidity of the soils under investigation and probably of most other acid soils of the same origin.

The form of aluminum immediately concerned in the unproductivity of acid soils in the soluble form, is the salts. These salts are derived from the acid-soluble aluminum hydroxide, or gibbsite. In soils sufficiently provided with calcium, toxic aluminum salts may never be formed, but in soils deficient in calcium and other bases, as in the case of acid soils, toxic aluminum salts are largely the end-products of sulfonation and nitrification.

It is not denied that iron and manganese may become contributing factors in the unproductivity of some acid soils, but the preponderance of evidence points to aluminum as the determining factor in the acidity of the soils under investigation.

The potassium nitrate extract of an acid soil is acid, but the same extract after sufficient amounts of limestone have been applied to the soil is alkaline.

In the first case an exchange of bases takes place between the aluminum compounds and the potassium-nitrate solution bringing aluminum into solution and forming aluminum nitrate, which on hydrolysis produces strong acidity. This is the cause of the acid reaction of the solution. In the second case an exchange of bases also takes place, but this time between the calcium compounds and the potassium nitrate solution, bringing calcium into solution and forming calcium nitrate. This compound is not hydrolyzed and therefore will not produce acidity. This explains the neutral or alkaline reaction of the extract.

In so far as aluminum is a factor in soil acidity the Hopkins method is the best one for soil-acidity determinations. It determines active aluminum and under field conditions when the lime requirement of the soil has been satisfied with the amount of calcium carbonate as determined by the method, the toxicity of aluminum is eliminated.

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PLATE 1

EFFECT OF ALUMINUM SULFATE ON THE GROWTH OF SWEET CLOVER

FIG. 1. First crop, 93 days old.

101—Control—plant-food only.

102—Plant-food plus 3100 pounds of $\text{Al}_2(\text{SO}_4)_3$ per acre.

103—Plant-food plus 620 pounds of $\text{Al}_2(\text{SO}_4)_3$ per acre.

104—Plant-food plus 15,500 pounds of $\text{Al}_2(\text{SO}_4)_3$ per acre.

105—Plant-food plus 3100 pounds of $\text{Al}_2(\text{SO}_4)_3$ per acre plus 2716 pounds of CaCO_3 .

106—Plant-food plus 3100 pounds of $\text{Al}_2(\text{SO}_4)_3$ per acre plus 543 pounds of CaCO_3 .

107—Plant-food plus 3100 pounds of $\text{Al}_2(\text{SO}_4)_3$ plus 13,580 pounds of CaCO_3 .

108—Plant-food plus 3100 pounds of $\text{Al}_2(\text{SO}_4)_3$ per acre plus 1054 pounds of CaCO_3 .

109—Plant-food plus 3100 pounds of $\text{Al}_2(\text{SO}_4)_3$ per acre plus 211 pounds of CaCO_3 .

110—Plant-food plus 3100 pounds of $\text{Al}_2(\text{SO}_4)_3$ per acre plus 5270 pounds of CaCO_3 .

FIG. 2. Second crop, 96 days old. The same as above plus CaSiO_3 and acid phosphate, reduced from 100 to 400 pounds per acre.



FIG. 1



FIG. 2

PLATE 2

EFFECT OF ALUMINUM CHLORIDE ON SWEET CLOVER

FIG. 1. Sweet clover at the age of 44 days.

201—Control—Plant-food only.

202—Plant-food plus 2405 pounds of AlCl_3 per acre.

203—Plant-food plus 461 pounds of AlCl_3 per acre.

204—Plant-food plus 12,025 pounds of AlCl_3 per acre.

205—Plant-food plus 2405 pounds of AlCl_3 plus 2716 pounds of CaCO_3 per acre.

206—Plant-food plus 2405 pounds of AlCl_3 plus 543 pounds of CaCO_3 per acre.

207—Plant-food plus 2405 pounds of AlCl_3 plus 13,580 pounds of CaCO_3 per acre.

208—Plant-food plus 2405 pounds of AlCl_3 plus 1054 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

209—Plant-food plus 2405 pounds of AlCl_3 plus 211 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

210—Plant-food plus 2405 pounds of AlCl_3 plus 5270 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

FIG. 2. Same, at the age of 93 days. Treatment, same as above.



FIG. 1



FIG. 2

PLATE 3

EFFECT OF ALUMINUM NITRATE ON SWEET CLOVER

FIG. 1. First crop, 93 days old.

301—Control—Plant-food only.

302—Plant-food plus 3859 pounds of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ per acre.

303—Plant-food plus 752 pounds of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ per acre.

304—Plant-food plus 19,295 pounds of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ per acre.

305—Plant-food plus 3859 pounds of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ plus 2716 pounds CaCO_3 per acre.

306—Plant-food plus 3859 pounds of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ plus 543 pounds of CaCO_3 per acre.

307—Plant-food plus 3859 pounds of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ plus 13,580 pounds of CaCO_3 per acre.

308—Plant-food plus 3859 pounds of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ plus 1054 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

309—Plant-food plus 3859 pounds of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ plus 211 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

310—Plant-food plus 3859 pounds of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ plus 5270 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

FIG. 2. Second crop, 96 days old. Same as above with the same changes as noted in series 100.



FIG. 1

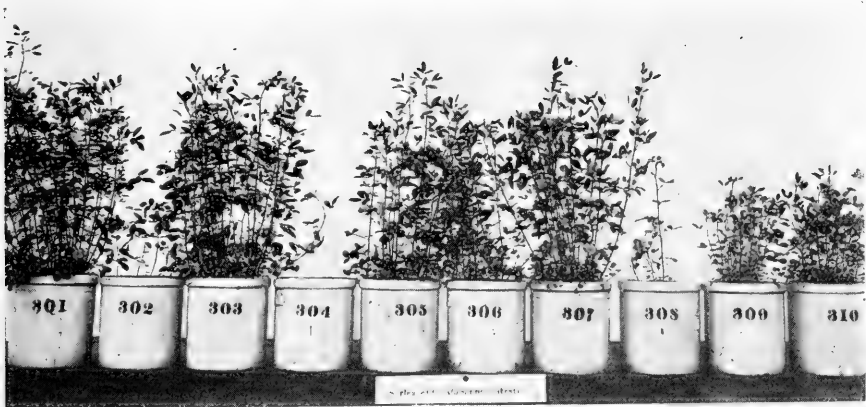


FIG. 2

PLATE 4

EFFECT OF ALUMINUM HYDROXIDE ON SWEET CLOVER

FIG. 1. First crop, 93 days old.

401—Control—Plant-food only.

402—Plant-food plus 1399 pounds of $\text{Al}(\text{OH})_3$ per acre.

403—Plant-food plus 280 pounds of $\text{Al}(\text{OH})_3$ per acre.

404—Plant-food plus 6995 pounds of $\text{Al}(\text{OH})_3$ per acre.

405—Plant-food plus 1399 pounds of $\text{Al}(\text{OH})_3$ plus 2716 pounds of CaCO_3 per acre.

406—Plant-food plus 1399 pounds of $\text{Al}(\text{OH})_3$ plus 543 pounds of CaCO_3 per acre.

407—Plant-food plus 1399 pounds of $\text{Al}(\text{OH})_3$ plus 13,580 pounds of CaCO_3 per acre.

408—Plant-food plus 1399 pounds of $\text{Al}(\text{OH})_3$ plus 1054 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

409—Plant-food plus 1399 pounds of $\text{Al}(\text{OH})_3$ plus 211 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

410—Plant-food plus 1399 pounds of $\text{Al}(\text{OH})_3$ plus 5270 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

FIG. 2-3. Second crop, 96 days old. Same as above up to 410 with the same changes as noted in series 100 to 300.

411—Plant-food plus 1399 pounds of $\text{Al}(\text{OH})_3$ plus 800 pounds of $(\text{NH}_4)_2\text{SO}_4$ per acre.

412—Plant-food plus 1399 pounds of $\text{Al}(\text{OH})_3$ plus 160 pounds of $(\text{NH}_4)_2\text{SO}_4$ per acre.

413—Plant-food plus 1399 pounds of $\text{Al}(\text{OH})_3$ plus 4000 pounds of $(\text{NH}_4)_2\text{SO}_4$ per acre.

414—Plant-food plus 6995 pounds of $\text{Al}(\text{OH})_3$ plus 800 pounds of $(\text{NH}_4)_2\text{SO}_4$ per acre.

415—Plant-food plus 1399 pounds of $\text{Al}(\text{OH})_3$ plus 800 pounds of $(\text{NH}_4)_2\text{SO}_4$ plus 2716 pounds of CaCO_3 per acre.

416—Plant-food plus 1399 pounds of $\text{Al}(\text{OH})_3$ plus 800 pounds of $(\text{NH}_4)_2\text{SO}_4$ plus 543 pounds of CaCO_3 per acre.

417—Plant-food plus 1399 pounds of $\text{Al}(\text{OH})_3$ plus 800 pounds of $(\text{NH}_4)_2\text{SO}_4$ plus 13,580 pounds of CaCO_3 per acre.

418—Plant-food plus 1399 pounds of $\text{Al}(\text{OH})_3$ plus 2423 pounds of dried blood per acre.

419—Plant-food plus 1399 pounds of $\text{Al}(\text{OH})_3$ plus 484 pounds of dried blood per acre.



FIG. 1



FIG. 2

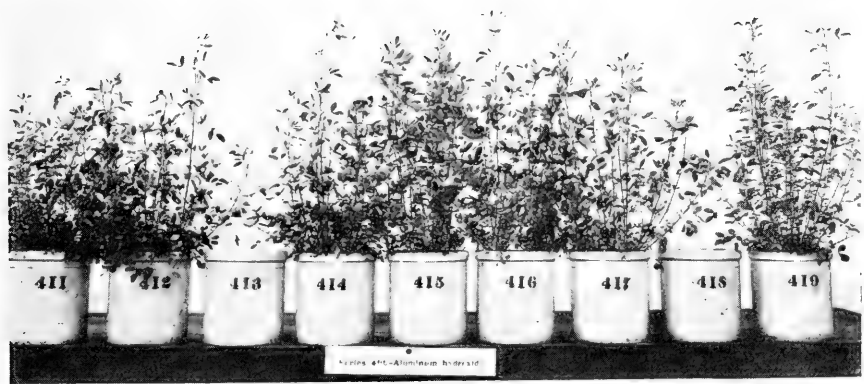


FIG. 3

PLATE 5

EFFECT OF ACID PHOSPHATE ON SWEET CLOVER

FIG. 1. First crop, 75 days old.

601—Control—Plant-food only.

602—Plant-food plus 964 pounds of $\text{CaH}_4(\text{PO}_4)_3$ per acre.

603—Plant-food plus 193 pounds of $\text{CaH}_4(\text{PO}_4)_3$ per acre.

604—Plant-food plus 4820 pounds of $\text{CaH}_4(\text{PO}_4)_3$ per acre.

605—Plant-food plus 964 pounds of $\text{CaH}_4(\text{PO}_4)_3$ plus 2921 pounds of CaCO_3 per acre.

606—Plant-food plus 964 pounds of $\text{CaH}_4(\text{PO}_4)_3$ plus 584 pounds of CaCO_3 per acre.

607—Plant-food plus 964 pounds of $\text{CaH}_4(\text{PO}_4)_3$ plus 14695 pounds of CaCO_3 per acre.

FIG. 2. Second crop, 67 days old. Amounts of acid phosphate reduced to from 100 to 400 pounds per acre.



FIG. 1



FIG. 2

PLATE 6

EFFECT OF LIMESTONE AND ACID PHOSPHATE ON THE PRODUCTIVITY OF GRAY SILT LOAM

FIG. 1. First crop, 98 days old.

701—Control.

702—2125 pounds of limestone per acre.

703—425 pounds of limestone per acre.

704—10,625 pounds of limestone per acre.

705—2310 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

706—462 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

707—11,550 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

708—2310 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 2125 pounds of limestone per acre.

709—2310 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 425 pounds of limestone per acre.

710—2310 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 10,625 pounds of limestone per acre.

FIG. 2. Second crop, 123 days old. Treatment, same as above.



FIG. 1



FIG. 2

PLATE 7

EFFECT OF LIMESTONE AND ACID PHOSPHATE ON THE PRODUCTIVITY OF YELLOW GRAY SILT
LOAM

FIG. 1. First crop, 98 days old.

801—Control.

802—2813 pounds of limestone per acre.

803—562 pounds of limestone per acre.

804—14,065 pounds of limestone per acre.

805—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

806—616 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

807—15,400 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

808—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 2813 pounds of limestone per acre.

809—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 562 pounds of limestone per acre.

810—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 14,065 pounds of limestone per acre.

FIG. 2. Second crop, 123 days old. Treatment, same as above.



FIG. 1



FIG. 2

PLATE 8

EFFECT OF LIMESTONE AND ACID PHOSPHATE ON THE PRODUCTIVITY OF YELLOW SILT LOAM

FIG. 1. First crop, 98 days old.

901—Control.

902—2921 pounds of limestone per acre.

903—584 pounds of limestone per acre.

904—14,605 pounds of limestone per acre.

905—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

906—616 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

907—15,400 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

908—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 2921 pounds of limestone per acre.

909—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 584 pounds of limestone per acre.

910—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 14,605 pounds of limestone per acre.

FIG. 2. Second crop, 123 days old. Treatment, same as above.



FIG. 1



FIG. 2

PLATE 9

SWEET CLOVER ON POTASSIUM-NITRATE AND WATER-LEACHED GRAY SILT LOAM SOIL

A. Water-leached soil.

A-1. Potassium-nitrate-leached soil.

A-2. Original soil plus KNO_3 equal to excess of KNO_3 in A-1.

A-3. Original soil.



PLATE 10

GRAPHS SHOWING THE DECREASE OF ACIDITY OF SOIL DUE TO TREATMENT — GRAY
SILT LOAM

Curve 1 represents the per cent decrease of acidity in 108 days; curve 2 the per cent decrease in 178 days.

701—Control

702—2125 pounds of limestone per acre.

703—425 pounds of limestone per acre.

704—10,625 pounds of limestone per acre.

705—2310 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

706—462 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

707—11,550 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

708—2310 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 2125 pounds of limestone per acre.

709—2310 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 425 pounds of limestone per acre.

710—2310 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 10,625 pounds of limestone per acre.

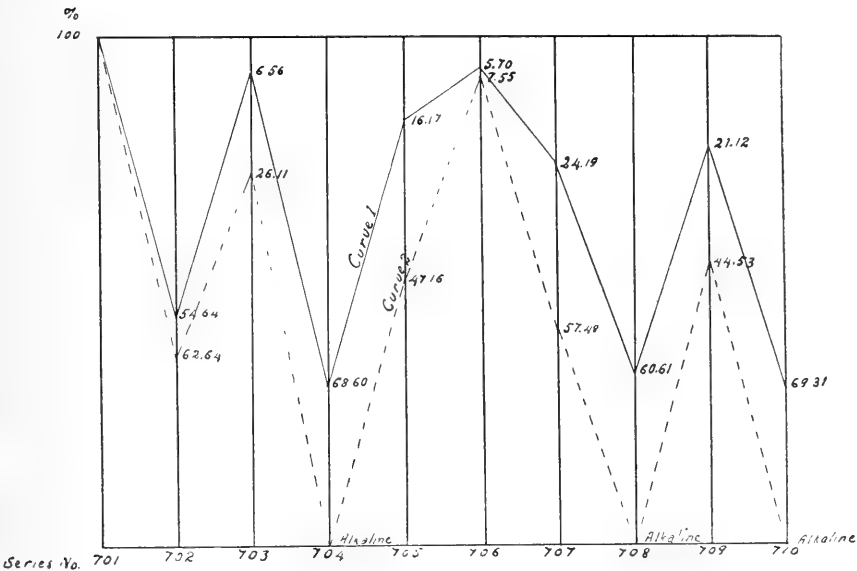


PLATE 11

GRAPHS SHOWING THE DECREASE OF ACIDITY OF SOIL DUE TO TREATMENT—YELLOW GRAY SILT LOAM

Curve 1 represents the per cent decrease of acidity in 108 days; curve 2 the per cent decrease of acidity in 178 days.

801—Control.

802—2813 pounds of limestone per acre.

803—562 pounds of limestone per acre.

804—14,065 pounds of limestone per acre.

805—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

806—616 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

807—15,400 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

808—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 2813 pounds of limestone per acre.

809—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 562 pounds of limestone per acre.

810—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 14,065 pounds of limestone per acre.

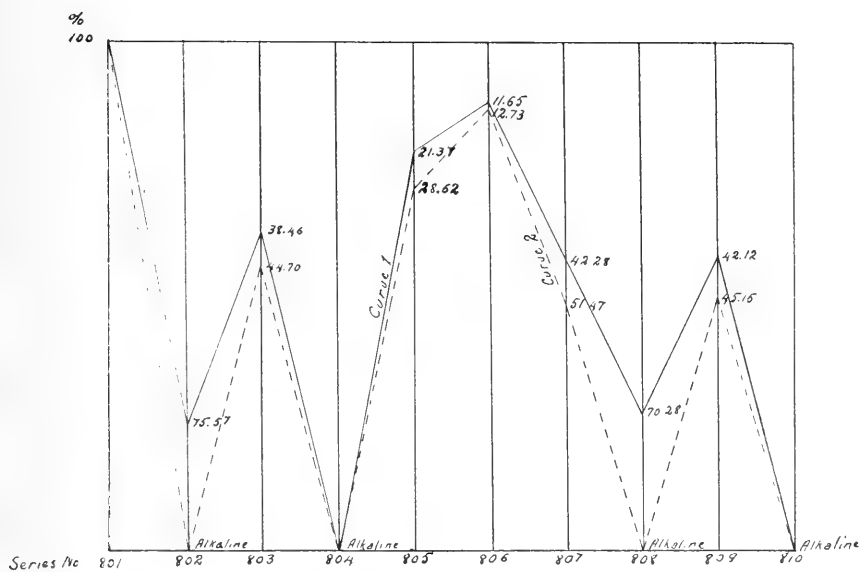


PLATE 12

GRAPHS SHOWING THE DECREASE OF ACIDITY OF SOIL DUE TO TREATMENT—YELLOW SILT LOAM

Curve 1 represents the per cent decrease of acidity in 108 days; curve 2 the per cent decrease of acidity in 178 days.

901—Control.

902—2921 pounds of limestone per acre.

903—584 pounds of limestone per acre.

904—14,605 pounds of limestone per acre.

905—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

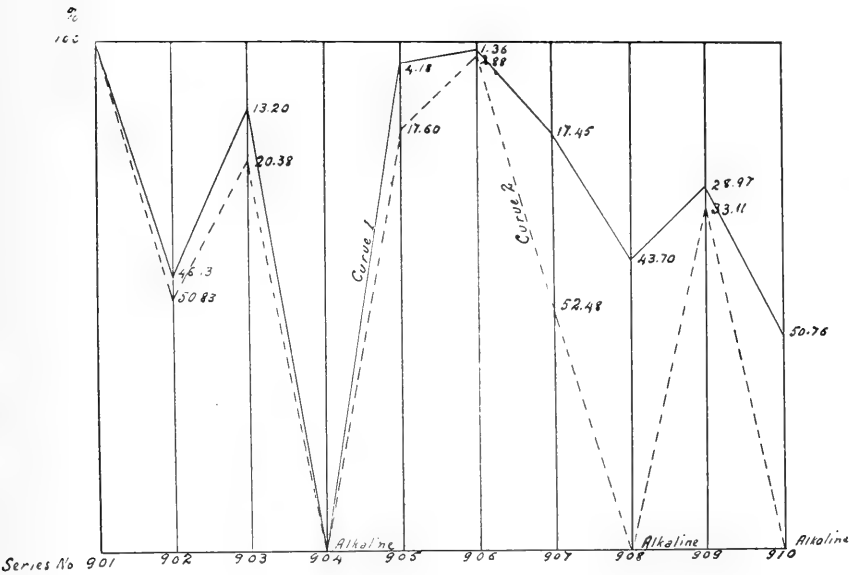
906—616 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

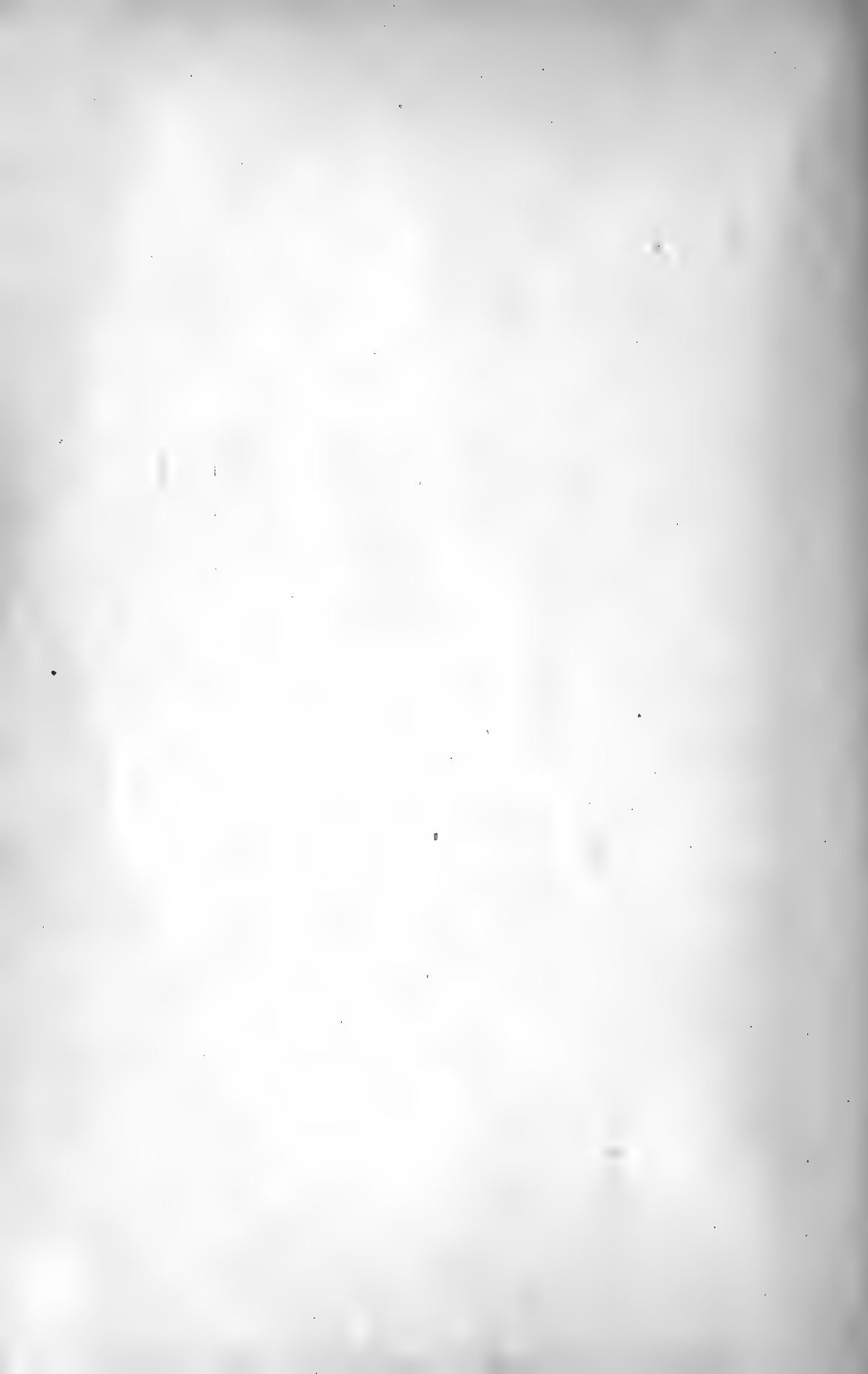
907—15,400 pounds of $\text{CaH}_4(\text{PO}_4)_2$ per acre.

908—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 2921 pounds of limestone per acre.

909—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 594 pounds of limestone per acre.

910—3080 pounds of $\text{CaH}_4(\text{PO}_4)_2$ plus 14,605 pounds of limestone per acre.





VITA

The author of this thesis was born in the town of Silay, province of Occidental Negros, Philippine Islands, April 19, 1891. He began his education in the private schools of the same town and in 1903 entered the public schools of Occidental Negros. From 1903 to 1907 he attended the primary and intermediate schools of Silay, and from 1907 to 1912 the intermediate and high schools of Occidental Negros, at Bacolod. After graduation in 1912 he entered the University of the Philippines as a provincial government student of Occidental Negros, graduating therefrom with the degree of Bachelor of Science in Agriculture, in 1915. His graduating thesis was: "Chemical Changes during the Ripening of Sugar Cane." He received the Master of Science degree in 1917, having as his thesis, "Spacing and Fertilizer Tests with Sugar Cane." From July, 1915 to February, 1916 he was employed in the College of Agriculture, University of the Philippines as a scholar assistant in Agronomy; from February, 1916 to August, 1916 as a graduate assistant in Agronomy; from August, 1916 to July, 1917 as assistant in Agronomy; and from July, 1917 to September, 1918 as instructor in Agronomy. In 1918 he was appointed by the Board of Regents of the University of the Philippines, a traveling Fellow for a period of two years, and entered the University of Illinois as a graduate student the same year. He was elected to the Illinois chapter of Sigma Xi in May, 1920.

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